

1929

I. Studies on the production of oxalic acid from corn stalks and cobs; II. Studies on corn stalk cellulose

Henry Albert Webber
Iowa State College

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I. STUDIES ON THE PRODUCTION OF OXALIC ACID
FROM CORN STALKS AND COBS.

II. STUDIES ON CORN STALK CELLULOSE

by

Henry Albert Webber

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

Iowa State College

1929

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PART I

STUDIES ON THE PRODUCTION OF OXALIC ACID FROM CORN STALKS AND COBS

I - INTRODUCTION

The object of this research was to ascertain if it is commercially feasible to manufacture oxalic acid from corn stalks and cobs. This study is in accord with the general trend of research carried on in the Chemical Engineering Department, Iowa State College, with the purpose in view of working up profitable by-products from the immense amount of agricultural wastes produced annually in the United States. These wastes include corn cobs and stalks, peanut shells, oat hulls, cottonseed hulls, wheat straw and similar materials.

It has been known for a long time that strong nitric acid under the proper conditions will oxidize certain types of aliphatic hydrocarbons to oxalic acid. Among these types are the sugars and celluloses. If the oxidation is continued too long the material being treated eventually goes to carbon dioxide, carbon monoxide, and water. Weaker concentrations of nitric acid produce various compounds depending upon the strength of the acid and the duration of treatment. Nitric acid under these conditions exercises a nitrating, hydrolyzing, and oxidizing action. Aromatic compounds, in general, when treated with strong nitric acid form nitrogen compounds.

5

The commercial importance of oxalic acid is probably best summarized by a short digest of an article by Kirkpatrick in Chemical and Metallurgical Engineering, July, 1926. Oxalic acid is one of the most important organic acids. Consumption in the United States at the present time is estimated at 6,000,000 to 8,000,000 pounds annually. This consumption depends more upon the price at which it is available than upon essential uses for which there are no substitutes. About 50 per cent of domestic consumption is by the laundries, which use it as an acid rinse. Chemical uses, including the production of various oxalate salts, account for 20 per cent, the dyeing and printing of textiles require 15 per cent and bleaching compounds 5 per cent. The remaining 10 per cent is used for miscellaneous purposes.

The United States Tariff Commission (35) in 1923 in connection with its investigation of oxalic acid made the following statement in regard to the transportation and distribution of oxalic acid:

"The chief markets for oxalic acid, which is largely handled by brokers and jobbers, are in New York and Chicago. The freight rate from Chicago, one point of manufacture, to New York City, is 56 1/2 cents per 100 pounds and from Niagara Falls (another producing center) to New York City is 26 1/2 cents. The inland and ocean freight from Rotterdam (center of Dutch industry) is about 22 cents per 100 pounds which is 34.5 cents less than the rate from Chicago to New York, and 4.5 cents per 100 pounds less than the rate from Niagara Falls to

the New York Market.

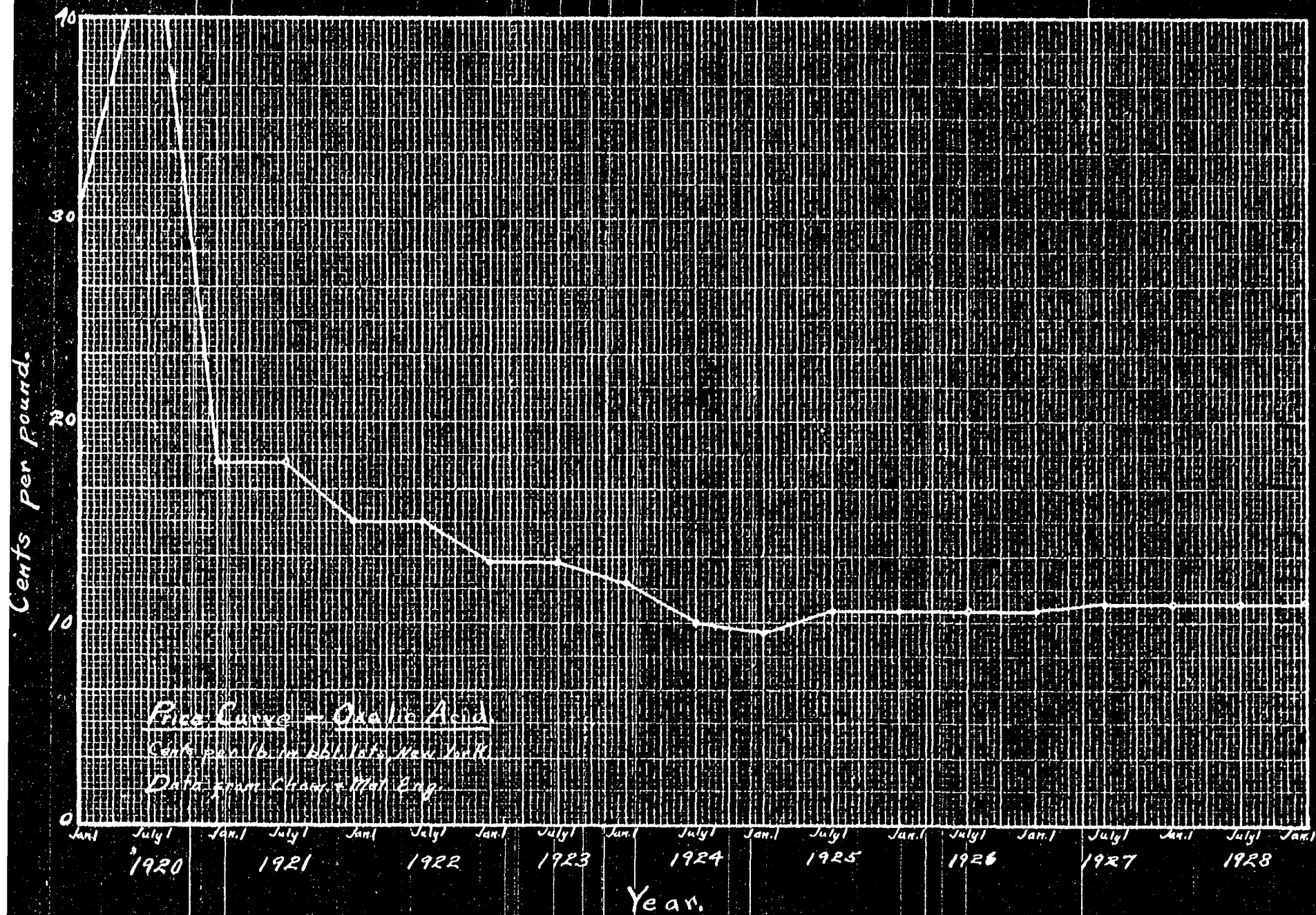
The price per pound of oxalic acid has varied in recent years from 7 to 8 cents per pound in 1914, through 70 cents per pound in 1916, then it steadily declined until from 1923 to 1925 it varied between 17 and 9 cents per pound. At present the quotations are 10 3/4 to 11 1/4 cents per pound."

It is believed that at present the only domestic producer of oxalic acid is the Victor Chemical Company of Chicago, Illinois. Their product is made by the formate method which in general consists in passing carbon monoxide over caustic soda under certain definite conditions of temperature and pressure. The process is carried on in two stages, the first at comparatively low temperature and high pressure yields sodium formate. As the pressure is released and the temperature raised two molecules of sodium formate unite to form sodium oxalate and hydrogen gas is evolved. The domestic product at present is protected by a duty of 6 cents a pound. This is necessary in order to meet strong competition from foreign producers, mainly Germany and Holland, who also use the synthetic formate process. Domestic production statistics are not available but in 1925, 2,569,275 pounds of oxalic acid were imported of which 80 per cent came from Germany.

An older process of manufacture was fusing sawdust with caustic potash, or with a mixture of caustic potash and caustic soda. The high cost of the potash rendered this method

unable to compete with the formate method when the latter became sufficiently developed. Research in this department has indicated that corn cobs when treated with caustic soda alone give almost as good results as when a mixture of caustic soda and caustic potash is used.

The idea of oxidizing corn cobs to oxalic acid with nitric acid was suggested by the work of several German chemists (1) who used sugar as the primary material. From one pound of sugar they obtained 1.4 pounds of oxalic acid. The initial cost of the sugar was the most serious handicap to this process. Since that time other chemists have used other materials such as starch, glucose, dextrin, gums, and cellulose, and have taken out patents covering various ways of treating the materials with nitric acid. The essential parts to this process are a very cheap raw material and satisfactory recovery of the nitric acid so it may be used over again. Further details regarding nitric acid recovery are given later in this thesis.



II - PREVIOUS WORK

OXIDATION WITH NITRIC ACID

Since corn cobs and stalks offer a cheap and abundant raw material, several studies have been made in this department using cobs in the nitric acid oxidation process. Cash and Sayler (2), Farlow (3), Prexel (4), and Webber (5) all worked on this problem. The work of the last three duplicated to some extent the work of the first two in the effort to find optimum conditions for the reaction. However, the latter students, profiting by the experience of the former, gradually increased the yields and gained further insight into the mechanism of the reaction. Outside the work done here there seems to be nothing in the literature regarding the use of cobs in this process.

In the effort to find optimum conditions the work so far has been confined mainly to finding the proper concentration of the acid to use, the best temperature, and the most effective catalyst. The studies of all the investigators are in good agreement as to the optimum conditions which are as follows:

(1) The nitric acid must be of the grade called "red fuming" and have a specific gravity of 1.50 or higher, (95% HNO_3).

(2) Five parts by weight of the above acid must be used for one part of cobs.

(3) Vanadium pentoxide or molybdic oxide, or a mixture of the two are the most effective catalysts.

(4) The reaction must be stopped at a certain point, which will be discussed later, in order to secure high yields.

(5) The products of the reaction must be allowed to stand without the addition of any water for two or three days to obtain a high yield.

The mechanism of the reaction in general is as follows: When the acid and catalyst are added to the cobs, the acid immediately begins to attack the cobs which are decomposed with much frothing and foaming in a vigorous reaction, accompanied by the evolution of large volumes of nitrogen oxides, in which the red fumes of nitrogen peroxide seem to predominate. The temperature of the mass rises to $60^{\circ} - 80^{\circ}\text{C}$. When the temperature has risen to this extent any unmoistened particles of cob present are apt to catch on fire. When ignition takes place the rest of the mass takes fire and all of it is apt to burn to a char. To prevent the contents from catching afire it is very necessary that the entire mass of cobs be moistened by the acid immediately after adding the acid. This can be done by stirring the mixture or by spraying the acid over all the cobs.

This vigorous decomposition of the cobs proceeds for several moments, then, when the cobs are almost completely in solution and the contents of the reaction vessel have the appearance of a dark brown liquid the reaction gradually sub-

sides. If no catalyst is present, no further vigorous reactions take place although there is a slow evolution of nitrogen oxides for a period of several days, and after several hours crystals of oxalic acid begin to separate out of the mother liquor. However, if a catalyst is present, soon after the cobs go into solution a very vigorous second reaction takes place. The brown liquid has the appearance of a boiling liquid, the brown fumes of nitrogen peroxide give way to a pale yellow mist and the liquid changes from a dark brown color to a greenish yellow mixture. This is the critical point of the whole reaction. The contents must be cooled immediately when this second reaction has started. Since the reaction is so violent, it is very hard to determine the exact point at which to start the cooling. The yields will vary by as much as 25% if the cooling is not started at the proper time. Equally as important as the proper moment to start cooling is the effectiveness of the cooling. The quicker the contents are cooled to 30° - 40°C the higher will be the yields. If the reaction is allowed to proceed to the stage where the contents have a greenish yellow appearance and the yellow mist is coming off, it has gone too far and the yields will be low. By the time this stage is reached there will have been a great loss of material and most of the cob will have been oxidized to carbon dioxide, carbon monoxide, and water.

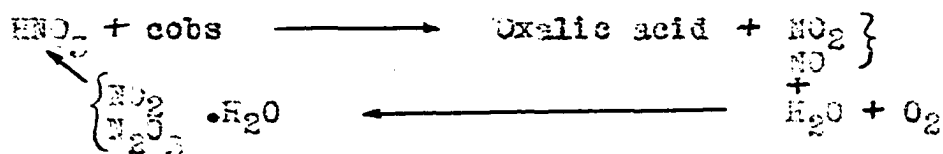
That this reaction is caused by the catalyst has been proved by adding the catalyst to a mixture of cobs and acid

long after the cobs have gone into solution. The vigorous second reaction invariably takes place after several minutes. The tendency of the catalyst to drive the reaction to completion with the formation of carbon dioxide, water and carbon monoxide necessitates that the reaction products after being cooled at the proper time be kept cooled with a water bath or other means for a day or two until the formation of oxalic acid crystals is well advanced. The cooling is effected by circulating water through coils in the reaction vessel, or by pouring water on the vessel or by submerging the vessel in a cold water bath. Plenty of water is necessary.

While the presence of a catalyst necessitates some precautions, as outlined above, much higher yields are obtained by using a catalyst. It was thought at first that strong heating from the very first increased the yield, but later it was shown that heating merely hastens the solution of the cobs and the start of the second reaction. In fact when the reaction vessel is heated externally the final solution of the cobs and the second reaction merge so closely into one stage that it is hard to differentiate between them. Equally as high yields can be obtained by dispensing with any external heating if a catalyst is present. External heating does hasten the reaction but since the entire reaction is so vigorous it is much easier to control if no heating is employed. Heating, without a catalyst, also gives good yields. In fact the writer

is of the opinion that external heating and the catalyst are interchangeable, and that either one gives as good results as the two when used together. The most important point is to get a temperature of 90° - 100° C. Without a catalyst or external heating the maximum temperature is 60° - 80° C. The presence of the catalyst will bring the proper maximum temperature and of course it can also be attained by heating the reaction vessel.

One of the apparent advantages of the nitric acid process for making oxalic acid from cobs is the fact that it is a cyclic process, the nitric acid being used over and over again in a scheme represented by the following diagram:

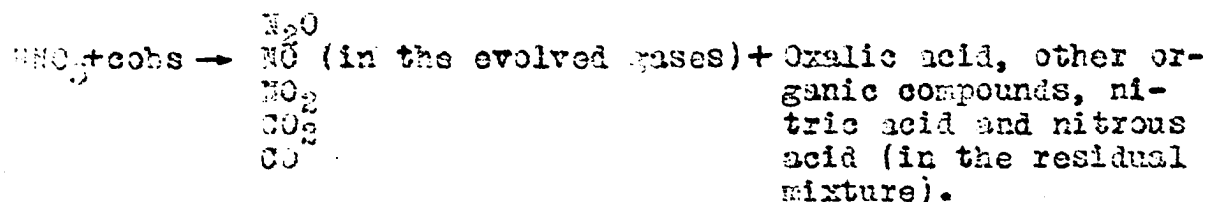


When HNO_3 is used as an oxidizing agent for organic substances the reduction products formed depend upon the concentration of the nitric acid and other conditions such as the temperature and the length of the heating period. In one case (18) where dilute nitric acid (10 per cent) was used, the gases evolved had the following composition:

<u>Constituent</u>	<u>Per cent by Volume</u>
N_2	18.3
H_2O	9.4
NO	9.3
NO_2	35.3
N_2O_5	8.3
CO_2	17.3
CO	4.3

When strong solutions of nitric acid are used the de-

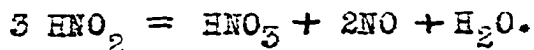
composition is not so severe and usually no free nitrogen is produced. Such a reduction can be illustrated as follows:



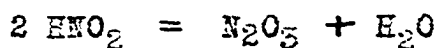
Nitrous oxide (N_2O) if formed would represent a loss of total nitrogen. It is soluble in water at 20°C to the extent of 0.6294 cc. (0°C and 760 mm.) per cc. water, but, while it is theoretically the anhydride of hyponitrous acid $\text{H}_2\text{N}_2\text{O}_2$, it does not form this acid by solution in water. Neither does it oxidize to the higher oxides of nitrogen at ordinary temperatures, being a highly endothermic compound. In ordinary absorption systems it is usually present to an extent of not more than 0.5 per cent, and does not interfere with the recovery of NO and NO_2 .

Any nitric oxide (NO) formed can be oxidized to NO_2 and, together with the NO_2 originally present, can be recovered as nitric acid to be used over again. Further details regarding the absorption of NO and NO_2 will be considered later in this thesis.

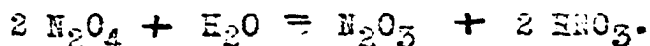
Considering the mother liquor there would be oxalic acid, nitrous acid (HNO_2) and nitric acid (HNO_3). It is likely that in this process no reduction to hydroxylamine takes place. The nitrous acid present decomposes according to the equation.



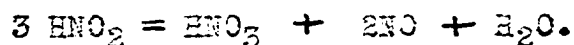
The reaction is reversible but by agitation with air the NO can be driven off and oxidized to NO₂. This represents the reaction when the solution is sufficiently dilute, as in the first towers of an absorption system. In more concentrated solutions the following reaction is more probable.



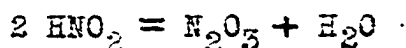
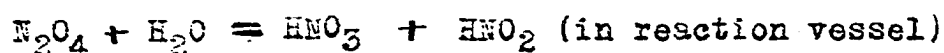
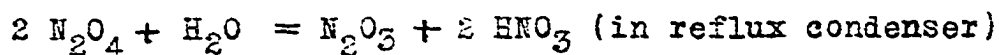
Since the liquor left in the reaction vessel immediately after cooling is relatively concentrated it seems more probable that the last reaction predominates. It has been observed that during the violent stages of the reaction a bluish-green liquor occurs in the reflux condenser. This is probably due to the reaction.



This liquor is continually draining back into the reaction vessel, but at the end of the reaction (that is, after cooling the vessel) a dark brown liquor remains. This is due to the liquor being saturated with N₂O₄ in excess of the quantity represented by the above equation. If this liquor is drenched at once with an excess of water, the mixture assumes a light yellow color, a light flocculent precipitate appears, and there is a brisk evolution of colorless gas. This evolution of gas is apparently produced by the reaction.



The reactions might be summarized in this manner



If the contents of the flask, whether drenched or not, are analyzed immediately after a run there is found to be no oxalic acid present. After several days standing if the contents have been drenched with water, there is still little oxalic acid to be found. If no water is added, however, after standing for several hours, crystals of oxalic acid begin to appear. An explanation of this fact might be that the cobs, after going into solution, are present as intermediate compounds soluble in the nitric-nitrous acid mixture. As the mixture stands a further slow oxidation goes on until the intermediate compounds are converted to oxalic acid. During this process the red fumes of NO_2 are being slowly given off. They may come off both as NO_2 directly and as NO , which is immediately oxidized to NO_2 when it strikes the air. Now if the solution of cobs is drenched immediately after a run some of the cobs revert to the flocculent white precipitate. This product is known as "xyloidine" and was first prepared by Braconnot (6) in 1833 from starch. The cobs remaining in solution as intermediate compounds are now in such a weak acid solution that evidently little or no oxidation to oxalic acid is able to take place.

III - EXPERIMENTAL WORK

A. Some Factors Influencing the Cyclic Nitric Acid Oxidation Process

Although, as the foregoing section indicates, there has been quite an extensive amount of work done on the process of oxidizing corn cobs with fuming nitric acid to produce oxalic acid the economics of this process have not been emphasized to any great extent.

This research, therefore, stresses the economic side of the process and the experimental work was outlined with three objects in view, namely; to improve the yield of oxalic acid per pound of cobs, to see if absorption of the nitrogen oxides and subsequent concentration of the dilute nitric acid could be eliminated from the cyclic process, and finally to ascertain if any of the nitric acid used was being reduced so far that it could not be recovered and used over again. The importance of ascertaining these facts will be discussed in detail.

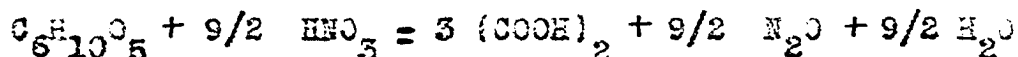
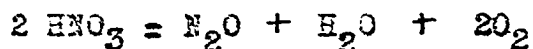
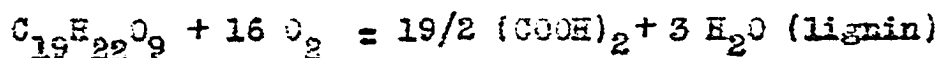
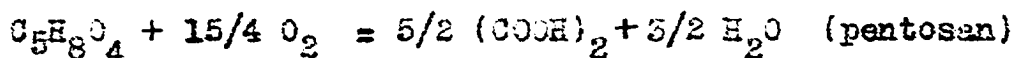
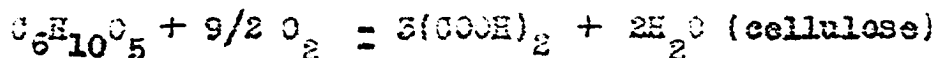
In the work done so far it has been found that five pounds of 1.5 HNO_3 per pound of cobs was the best ratio to use. Some theoretical considerations were made based on this fact in order to find out to what stage the HNO_3 used was being reduced, and also to find out what was doing the oxidizing, the nitrogen peroxide or the nitrogen pentoxide. These considerations are as follows:

Theoretical amount of HNO_3 per pound of cobs:

(assuming the cob is 35 per cent cellulose, 27 per cent

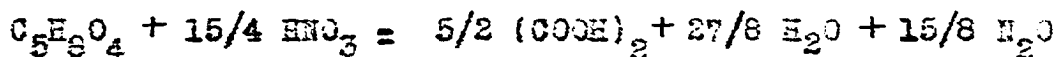
pentosan and 33 per cent lignin)

Reactions:



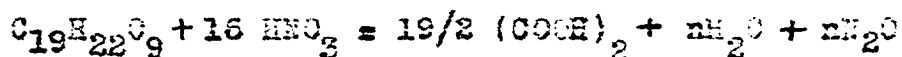
$$162 : 283.5 = 0.35 : x$$

$x = 0.61$ lbs. HNO_3 for the cellulose



$$132 : 236.25 = 0.27 : x$$

$x = 0.48$ lbs. HNO_3 for the pentosan

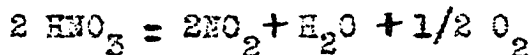
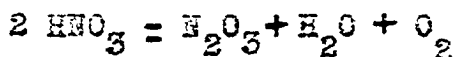
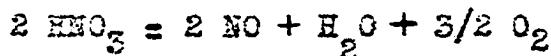


$$594 : 1008 = 0.33 : x$$

$x = 0.84$ lbs. HNO_3 for the lignin

Total HNO_3 required per pound of cobs when the HNO_3 is entirely reduced to $N_2O = 0.61 + 0.48 + 0.84 = 1.93$ lbs.

Similar calculations for the reactions



give, together with the preceeding result, the following tabulation:

HNO_3 (N_2O , H_2O) reduced 5 to 2	Lbs. HNO_3 required per lb. of cobs
N_2O	1.93
NO	2.57
H_2O_3	5.86
NO_2	7.72

These figures show that if 5 pounds of HNO_3 per pound of cobs is the correct ratio, evidently the HNO_3 is being reduced to N_2O_3 which would leave a mixture of HNO_3 and HNO_2 in the liquid residue and cause an equimolar mixture of NO_2 and NO to pass off in the gases evolved. Actual analysis of the gases shows that the ratio of NO_2 to NO is much higher than this. Any N_2O produced is very undesirable as it represents a loss of nitrogen. If all the HNO_3 used is reduced to NO it would take about three pounds of HNO_3 per pound of cobs. This would be highly satisfactory but actually it does not take place. In the majority of reactions where 1.5 HNO_3 is used as an oxidizing agent the predominating oxide given off is NO_2 with lesser amounts of NO . This seems to be the case in the reaction under consideration. Hence it seems improbable that a ratio smaller than 4 1/2 or 5 to 1 can be used. However, other agencies might be introduced which would cause a greater reduction to NO with a correspondingly smaller amount of HNO_3 used. Some of these will be considered later.

If it is assumed that the ratio, 5 pounds of HNO_3 to 1 pound of cobs, is the minimum that can be used, the importance of the three foregoing objectives can be developed.

The best yield of oxalic acid obtained so far is one pound of oxalic acid from one pound of cobs. If, by proper control, this yield could be duplicated in each batch in a commercial process, the following cost considerations can be

estimated.

The cost of the cobs is estimated at \$10.00 per ton or 1/2 cent per pound. The present value is about \$2.00 per ton.

The cost of producing 90-95% HNO_3 is given by F. C. Zeisberg of E. I. du Pont de Nemours Co. (Chem. and Met. Engr. Vol. 24, No. 10, March 9, 1920) as follows:

Normal cost per 100 lbs. HNO_3

Labor	0.06
Repair Labor	0.06
Retorts	0.08
Supplies	0.05
Fuel	0.03
Power	0.05
Overhead	0.18
	<u>0.49</u>

Less credit for niter cake 0.24

0.49 - 0.24 = 0.25 production cost
 145 lbs. NaNO_3 at 2.5¢ = 3.63
 151 lbs. H_2SO_4 at 1¢ = 1.51
 Total Cost = 5.39 per 100 lbs. HNO_3 or about
 5.4 cents per pound of HNO_3 .

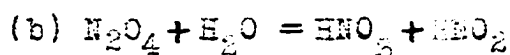
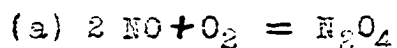
This represents a 99% yield of 90-95% HNO_3 from the pot process for making HNO_3 .

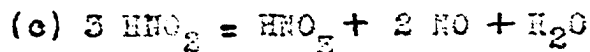
If five pounds of HNO_3 are used per pound of cobs the cost of the acid would be $5 \times 5.4 = 27$ cents, but since the process is cyclic this cost would be eliminated after the process is "tuned up" and the actual acid cost thereafter would comprise the cost of operating an acid recovery system plus the make-up acid needed to balance any loss of acid in the cyclic process.

This process could follow to some extent the general procedure of nitro-cellulose manufacture: that is, the cobs would be converted to oxalic acid in suitable reaction vessels, the nitrogen oxides given off would be absorbed in towers and reconverted to strong nitric acid, the crystals of oxalic acid after separating out of the mother liquor would be centrifuged out and washed, and the wash liquor together with the mother liquor would enter the absorption towers as weak nitric acid. The nitrous acid in the mother liquor could be converted to nitric acid by agitation with air and raising the temperature slightly. The catalyst could be recovered by filtration and used over again.

Such a process, however, requires that certain conditions must be met. These are as follows: the cost of recovering the acid must not be too great, and the per cent of unrecoverable acid must not be above a certain maximum. Both the cost and efficiency of an absorption system depend to a great extent upon the composition of the gases to be recovered. The richer the gases are in NO_2 the less is the cost of recovery, and the greater is the per cent recovered. The reasons for this are as follows:

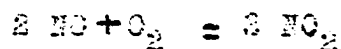
If we consider the gaseous phase in an absorption system the reactions are



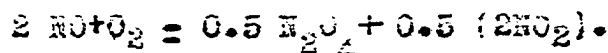


(d) $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$ and so on until the NO is entirely changed to N_2O_4 and absorbed or else is lost in the exit gases.

Reaction (a) or (d) is the one requiring the longest time and is the one upon which the capacity of the system depends. Richardson (7) found that the reaction



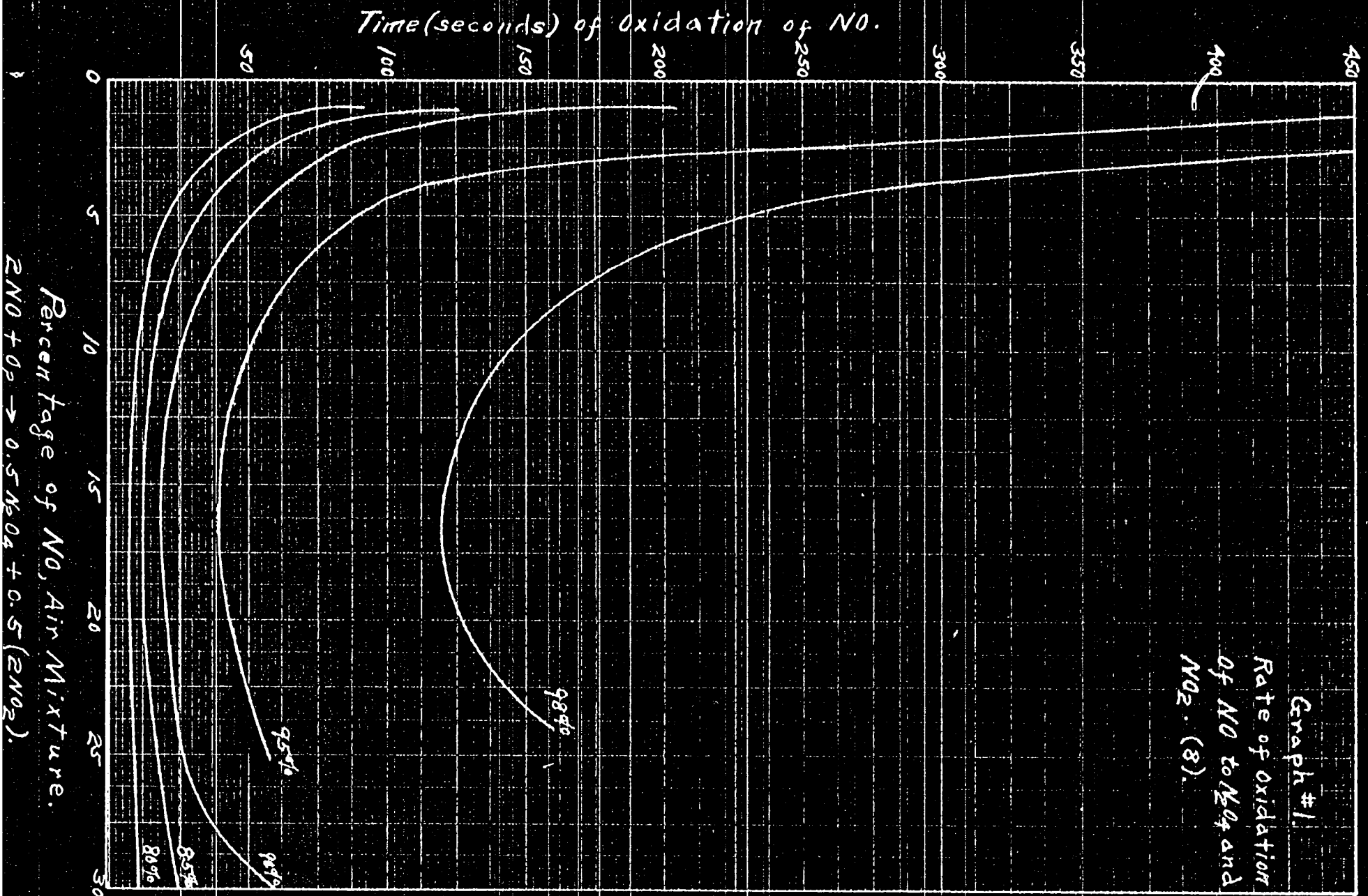
goes to the right only at temperatures below 140°C . Decomposition into NO and O_2 sets in above this temperature and at 620°C the NO is completely decomposed. The following graph (#1) due to Lunge and Berl (8) shows the time in seconds required to bring various mixtures of NO and air to different stages of oxidation, calculated on the assumption that the nitrogen tetroxide is half dissociated and therefore that

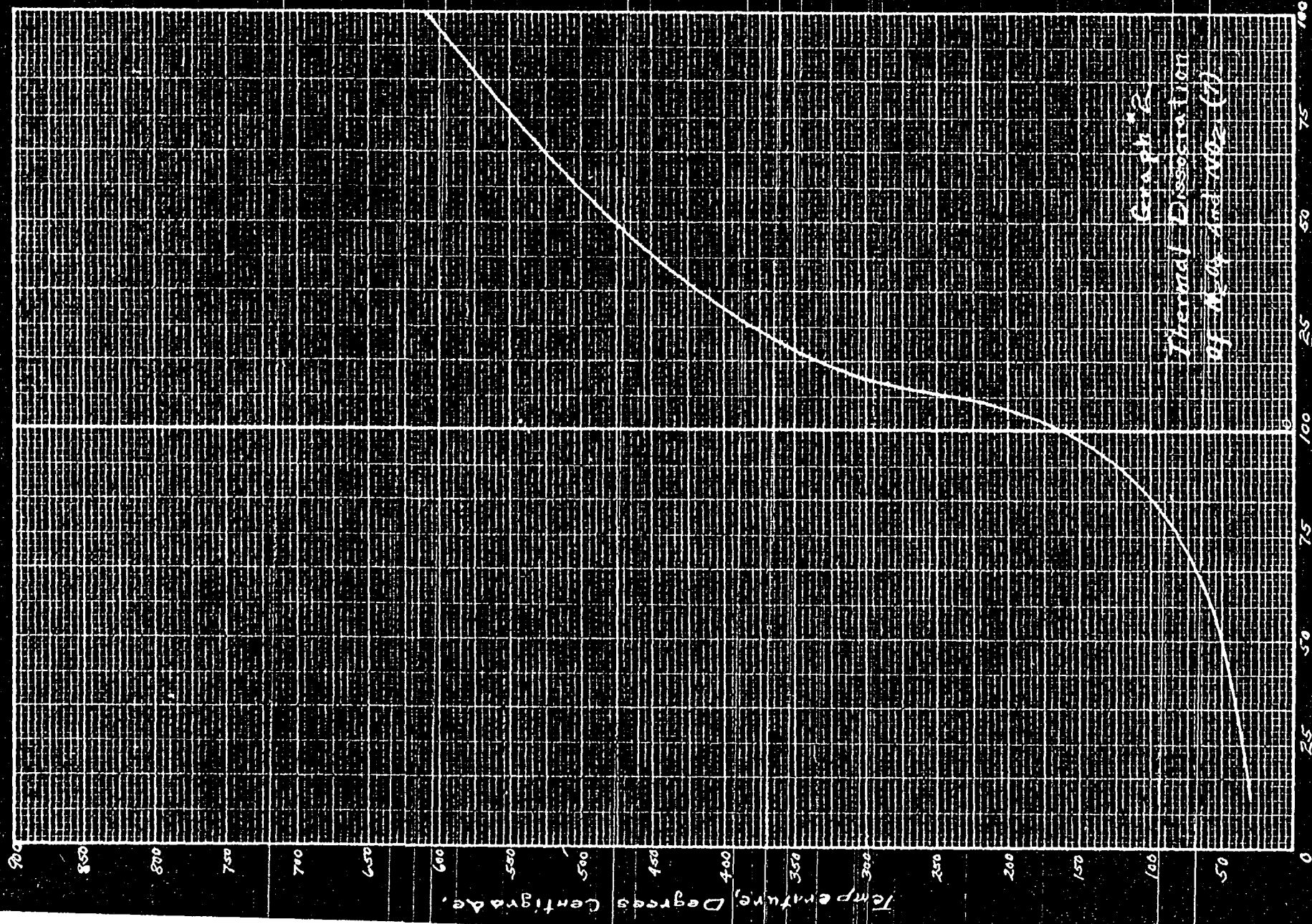


This corresponds to a temperature of about 60°C . as shown by the second graph. (#2).

The first graph indicates that the most rapid oxidation occurs when the percentage of NO in the mixture NO - air is between 17-20 per cent, and also that the minimum time for the various mixtures depends upon what stage of oxidation is reached e.g. 80 per cent of the NO in a 20 per cent mixture of NO and air requires a shorter time to oxidize than 80 per cent of the NO in a 17.5 per cent mixture, but 95 per cent of

Graph #1.
Rate of oxidation
of NO to NO_2 and
 $\text{NO}_2 \cdot (8)$.





Per Cent N_2O_4 Dissociated

Per Cent NO_2 Dissociated

Into NO_2 .

Into NO And O_2 .

a 17.5 per cent mixture requires less time to oxidize than 95 per cent of a 20 per cent mixture.

The effect of the oxidation of NO on the capacity of an absorption system is illustrated by comparison of the towers used in the arc process, the ammonia oxidation process and in denitrating processes. The percentage of NO in gases from the arc process is about 1 per cent by volume and about 5000 cubic feet of tower space are required to oxidize one pound of NO to NO₂ and absorb it as dilute nitric acid. In this process, towers 70-80 feet high and 10-20 feet diameter are commonly used. In ammonia oxidation processes, where the volume of NO in the gases is from 6-7 per cent, the towers are usually 50-60 feet high and 6-10 feet diameter. Large towers are more efficient than small towers and the capital cost per cubic foot of absorption capacity is less in about the ratio of 1 : 1.75 under normal conditions of labor and material costs, but since these large towers must be made of acid proof brick or stone, such as granite, and must be laid out with great attention to detail and require elaborate accessories, the initial outlay required runs into several hundred thousand dollars for a system of several towers in series. The gases from denitrating processes are much richer in NO and NO₂ than the gases in the two preceding processes, and therefore, much less tower capacity is required, and small stoneware units are used instead of the costly brick towers. To absorb one

pound of NO_2 per minute from a gas containing 15 per cent NO_2 requires approximately 120-150 cubic feet of tower space, while to effect the same amount of absorption with a gas containing one per cent NO_2 by volume requires more than 5000 cubic feet. Stoneware units cannot be used for large towers because they do not possess sufficient strength to resist a large amount of crushing weight or lateral pressure. Hence they are only suitable when the gases to be absorbed are relatively rich in NO (or NO_2). A set of eight stoneware towers in series, which is standard practice, 5 feet in diameter and from 12-15 feet high will yield 25-30 tons of nitric acid (as 100 per cent) per week of 168 hours, when dealing with a nitrous gas containing 12-15 per cent NO_2 , but with a gas containing only 2 per cent NO_2 the amount recovered will be less than 2 tons per week. This illustrates very clearly how capacity is influenced by the richness of the gas. Allowing 120-150 cubic feet of tower space for 1 pound of NO_2 per minute and using a scientific packing material giving 70 per cent free space, the free space required for 1 pound of NO_2 per minute would be about 90 cubic feet. The cost of erection of a set of eight such towers would be around \$10,000 at a maximum (10). This system would recover 30 tons of HNO_3 (as 100 per cent) per week or 1500 tons per year, from gases containing 12-15 per cent by volume of NO_2 . The capital cost per ton per year would therefore, be about \$6.70.

Some actual capacities and efficiencies obtained in

practice are as follows. (11):

	A	B
Composition of inlet gases	NO ₂ = 55% O ₂ = nil	NO ₂ = 15% O ₂ = 8%
Temperature of inlet gases	35° to 45° C	45° C
Reaction time	260 seconds	120-140 seconds
Power free space	1 lb. NO ₂ per minute per 100 cu. ft. free space.	1 lb. NO ₂ per minute per 120 cu. ft. free space.
Area of wetted surface	1 lb. NO ₂ per minute per 6000 sq. ft. of wetted surface.	1 lb. NO ₂ per minute per 5000 sq. ft. of wetted surface.
Efficiency of absorption	97 per cent	91 per cent

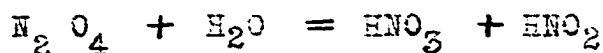
It is common practice in water absorption systems to recover about 90% of the total fixed nitrogen as HNO₃. The balance of the NO₂ and NO is recovered in the last tower through which an alkaline absorbent is circulated. However, in present day absorption practice, even when using a final alkaline absorbent, the efficiency obtained does not exceed 97-97.5 per cent as a maximum, calculated on the basis of total fixed nitrogen recovered. The 2.5-3 per cent loss obtained includes a handling loss of about 1 per cent, the remainder being due to the escape of HNO₃ mist and unabsorbed NO from the system. Where no final alkaline absorbent is used, the efficiency of the absorption system lies between 92-95 per cent if fairly concentrated nitrous gases are available. In this case the loss due to acid mist is between 2.5-3 per cent of the

total output of the towers. So far the only way discovered to recover the acid mist is by the use of a high-tension electric discharge apparatus such as the Cottrell electric precipitator. This necessitates a rather expensive installation.

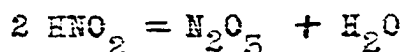
It has been stated before that gases containing 1-1.5 per cent by volume of nitrogen oxides require 5000 cubic feet of tower space per pound of NO_2 absorbed per minute, whereas gases containing 12-15 per cent nitrogen oxides require only 120-130 cubic feet of tower space and gases of 53% NO_2 require about 100 cubic feet of tower space per pound of NO_2 absorbed per minute. In general the concentrations of nitrogen oxides available from denitrating processes in the explosives industry are between 15-20 per cent, with an efficiency of recovery of about 96-97 per cent. In the process of oxidizing corn cobs with nitric acid to produce oxalic acid the gases are much richer in nitrogen oxides than those from any denitrating process and therefore would require less than 100 cubic feet of tower space per pound of NO_2 absorbed per minute. This would decrease the capital cost per ton of nitric acid recovered. In the second step of the process, that of recovering the mother liquor, it has been suggested that denitration could be eliminated by adding the mother liquor to the absorption system as part of the absorbing medium. Several complications are possible if this is done. If the mother liquor is circulated in the last towers without being diluted, the con-

centration of HNO_3 in it is so great that absorption of the nitrogen oxides will be inefficient.

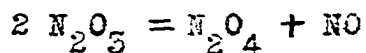
If the mother liquor is diluted and then added there will be a loss of NO for this reason: it has been observed that when good yields of oxalic acid have been obtained, after the first reactions there remains a brown liquid from which crystals of oxalic acid begin to separate out after several hours. Brown fumes of NO_2 come off for several days and after 2 or 3 days (at which time the oxalic acid crystals are removed) there still remains a mother liquor colored brown with dissolved NO_2 . If this mother liquor is diluted with water, the NO_2 dissolves to form a mixture of nitric and nitrous acid.



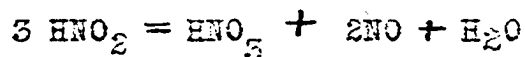
If the dilution is small the nitrous acid reacts as shown



and the N_2O_3 exists in equilibrium with NO and N_2O_4



If excess of water is added the reaction is then



Since NO is only slightly soluble in water some of it will be lost in the exit gases. If the mother liquor is added to the system in the first towers the same reactions take place. It would be necessary to dilute the mother liquor

as otherwise the efficiency would be low. Even if the liquor is diluted, with evolution of NO , the NO would be oxidized to NO_2 and recovered as dilute HNO_3 further on in the system. This therefore, would seem to be the logical way to dispose of the mother liquor and the process of denitration could be dispensed with. In order to avoid loss of nitrogen oxides during the centrifuging off of the oxalic acid crystals it would be necessary to have the centrifuges in an enclosed place with a draft leading to the absorption system. Furthermore, there is always some oxalic acid left in the mother liquor. If this was introduced into the absorption towers it might give rise to complications that would be detrimental to successful operation. It would also represent a loss of valuable oxalic acid. (See Table I for solubilities).

Probably the best way to handle the mother liquor would be to blow air through it, after crystallization of the oxalic acid had taken place, until all NO_2 and NO had been driven out, then centrifuge the crystals out of the remaining nitric acid solution, and distill off the nitric acid from the remaining oxalic acid in vacuo. This would leave a residue of oxalic acid, catalyst, and probably some nitrated cob pulp. These could be easily separated by dissolving out the oxalic acid, while the cob pulp and catalyst would go into a new batch. All wash water would go into the absorption system, and the air used in blowing the mother liquor together with the

Table I.

Solubility of Oxalic Acid in Nitric Acid Solutions.

Solubility at 15°C.		
$C_2H_2O_4 \cdot 2H_2O$	HNO_3	
Parts by wgt.	Parts by wgt.	Sp. Gr.
9.46	100	1.00
3.06	"	1.20
2.57	"	1.30
2.76	"	1.40

Solubility at 25°C.

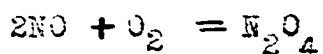
Mols per Liter

HNO_3	$H_2C_2O_4$
0.000	1.181
1.032	0.894
2.962	0.703
4.676	0.605
5.914	0.554
7.380	0.530
9.054	0.495
9.830	0.502
11.798	0.528
11.778	0.537
14.064	0.708

NO_2 and NO that it would pick up would also go into the absorption towers.

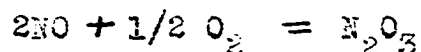
As stated previously, the fumes coming off from the reaction during its first and violent stages are very rich in NO_2 and NO , and therefore, can be easily and efficiently absorbed as dilute HNO_3 in relatively small towers. The fumes coming off slowly during the period of crystallization are also rich and can be readily absorbed. However, if the mother liquor is gassed with air to remove the dissolved NO_2 and NO , this would mean that a relatively dilute gas would enter the absorption system requiring a large tower capacity and decreasing the efficiency of the system. It would seem best therefore to arrange the system so that the air from a batch that was being gassed would enter the towers at the same time that the fumes from several batches in the first violent stages of reaction would be entering the towers. The air would then supply the O_2 necessary to oxidize the NO to NO_2 . The O_2 is usually supplied automatically by the air lifts in elevating the nitric acid from the bottom of one tower to the top of the tower next in line. The introduction of air from this new source might necessitate doing away with air lifts and using acid resistant pumps in their place. At any rate an excess of air is to be avoided as dilution of the nitrogen oxides would cause a decrease in efficiency of absorption, necessitate larger towers, and lower the concentration of the HNO_3 obtained.

It was shown on a previous page that the reaction

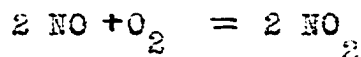


is the main reaction in an absorption system, because of its slowness, and limits the capacity of a system. Nitric oxide (NO) is only slightly soluble in water and it must be oxidized to N_2O_3 or NO_2 (N_2O_4) before it can be absorbed by water to form dilute nitric acid. It has also been shown that the time of oxidation varies considerably with the concentration of nitric oxide in the gas mixture. For example, a mixture containing initially 20 per cent of nitric oxide requires 19 seconds for 90 per cent oxidation, whereas a mixture containing initially 1 per cent NO requires 204 seconds for a similar amount of oxidation, and a gas containing 2 per cent NO requires 120 seconds for a 90 per cent oxidation.

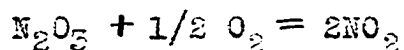
When there is an insufficient supply of oxygen, the oxidation of NO corresponds to the reaction



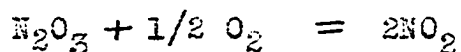
If plenty of oxygen is available the reaction is



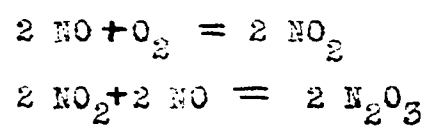
N_2O_3 can also be oxidized to NO_2



There has been some question regarding the steps in the oxidation of NO. Some investigators maintain that the steps are

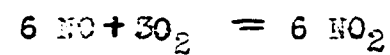


but it is generally agreed upon now that the correct stages are

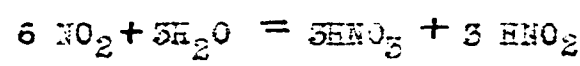


At atmospheric pressure (760 mm.) the proportion of undissociated N_2O_3 present comprises 3 per cent of the gas mixture. It is an advantage in some ways to have the NO oxidized completely to NO_2 in the absorption system as it decreases the load on the system in the following manner.

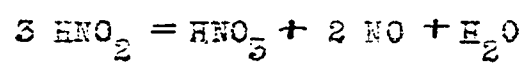
When NO is oxidized to NO_2



the NO_2 reacts at once with water to form nitric acid



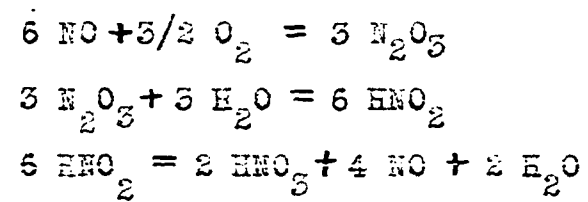
the HNO_2 breakdown immediately



and the NO formed is again oxidized to NO_2 and goes through the same cycle again.

Thus each time NO is oxidized to NO_2 two-thirds of the total nitrogen goes to HNO_3 .

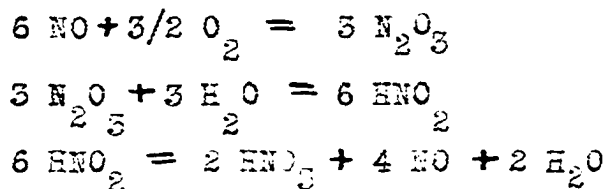
If the NO is only oxidized to N_2O_3 , the N_2O_3 reacts with water



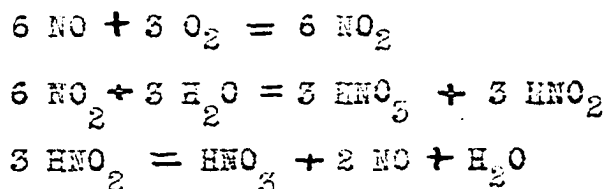
and only one-third of the total nitrogen goes to HNO_3 . There-

fore the load on the system is doubled.

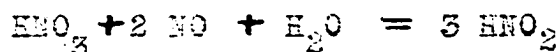
The oxidation of NO to NO₂ does not take place immediately and is hindered by a large amount of water, although some moisture is necessary. Hence, it is necessary to provide free unwetted space for the oxidation, and this is provided by large gas mains and unwetted oxidation towers. If the NO is with-drawn each time from the absorption tower and completely oxidized to NO₂ in an oxidation tower, the per cent of NO in a gas can be reduced from 66.7 per cent of its original volume to 2.5 per cent by a passage through 4 absorption towers in series. These extra oxidation towers are expensive however, and so a compromise is reached in commercial practice by providing large gas mains between towers to allow only for oxidation to N₂O₃. As shown before this should double the load on the system, but the breaking down of the HNO₂ formed to HNO₃ and NO is so much faster than the oxidation of NO to NO₂, that the capacity of the system is not decreased. In other words the cycle



is so much faster than the cycle



that the total capacity of a system is not decreased by the incomplete oxidation of NO to NO₂. Actually some of the NO goes beyond N₂O₃ to N₂O₄ and this decreases the number of towers necessary. However, the gas entering the system should contain only NO₂ molecules as any NO present will have a reducing effect on the relatively strong nitric acid circulating in the first tower,

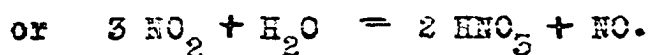
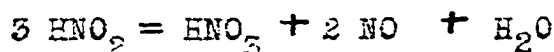


and also NO₂ is more readily taken up by both water and dilute nitric acid than is N₂O₃, which would be present if both NO and NO₂ were in the gas inlet mixture.

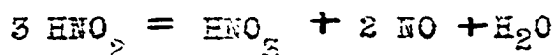
It is necessary to cool the nitrous gases from the reaction vessel before allowing them to enter the tower system. Graph #2 shows the thermal dissociation of N₂O₄ and NO₂. Thus at 64°C one-half the NO₂ is present as N₂O₄, while at ordinary temperatures (15°C) about 15 per cent of NO₂ is present as NO₂ and 85 per cent as N₂O₄. N₂O₄ is much more soluble in water than NO₂, so the greater the proportion of N₂O₄, the more readily is dilute HNO₃ formed by absorption. Good practice is to cool the gases below 40°C before allowing them to enter the towers.

Theoretically it is impossible to produce a nitric acid stronger than about 70 per cent (actually 68.4) by absorption of NO₂ in water. The following graph, #3, shows that at about 70 per cent the amount of NO₂ absorbed as HNO₃ is a

maximum. Further gassing of the absorbent with NO_2 causes the NO_2 to go into solution as HNO_3 but not as HNO_2 according to the reaction

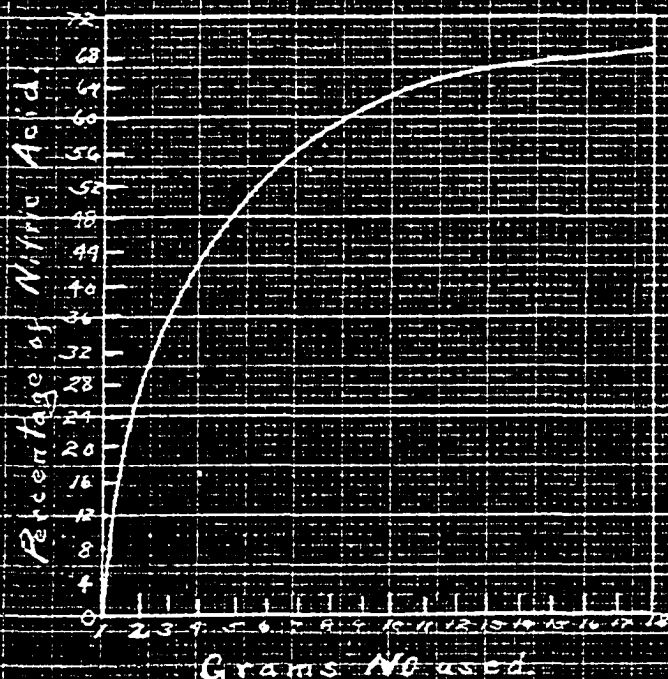


At this concentration (68.4) the effect of the NO liberated by the decomposing HNO_2 is to drive the reaction to the left and thus prevent any further increase in concentration of HNO_3 . The decomposition of HNO_2 into HNO_3 and NO



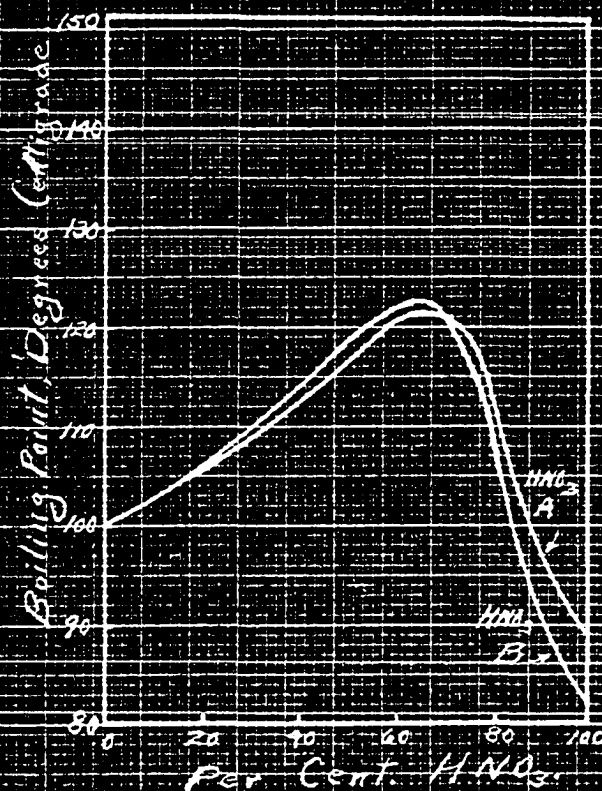
when either N_2O_5 or NO_2 is absorbed in water or dilute HNO_3 explains why an efficiency of only 90-92 per cent is reached unless either an excessive number of towers (theoretically an infinite number) is used or else an alkaline absorbent is circulated in the last tower. In this case nearly all the NO present will be removed (with an equivalent of NO_2) as N_2O_5 , without the regeneration of nitric oxide. In large scale plants, handling dilute gases, the longest period allowed for the gases to traverse the absorption system is twenty minutes. In smaller tower systems, using gases richer in NO, less time is required.

Not only does the per cent of NO in the inlet gases affect the efficiency and capacity of an absorption system but it also determines the concentration of HNO_3 obtained from the towers. Theoretically an acid of about 70 per cent strength



Graph #3.

Rate of increase in concentration of HNO_3 produced by passing Nitrous Gases thru water.



Graph #4.

Boiling Points of Nitric Acid of different concentrations.

A--Creighton and Githens.

B--Pascal.

is possible, but actually this can be obtained only under the most favorable conditions, such as can be made to prevail in the laboratory. A gas mixture containing 1 per cent by volume of NO can be made to yield an acid of only 45-46 per cent HNO_3 . A mixture containing 7 per cent NO will yield 58-60 per cent HNO_3 as a maximum, and 60 per cent acid is the final product in most tower systems handling even relatively rich gases.

From the curve in graph #3 it is evident that the rate at which NO_2 is absorbed by nitric acid containing 60 per cent HNO_3 to form 64 per cent HNO_3 for example, is only about one-third of the rate at which the peroxide is absorbed by 56 per cent HNO_3 to form 60 per cent HNO_3 . Therefore, trying to obtain a 64 per cent HNO_3 instead of a 60 per cent acid cuts down the capacity of the system one-third. The extra absorption space required if the same output is to be maintained at 64 per cent HNO_3 instead of 60 per cent HNO_3 will be nearly twice the original. Also the reduction of nitric acid by NO is more rapid, the more concentrated the nitric acid, and the greater the mass of nitric acid present. At equilibrium, the ratio $\text{HNO}_3 / \text{HNO}_2$ was shown by Veley (9) to be about 15.5.

It has been found that the maximum percentage concentration of nitric acid obtainable by leading NO_2 (as N_2O_4) at temperatures above 0°C into water is 68.4 per cent HNO_3 at one atmosphere pressure. This is also the composition of

the mixture of nitric acid and water which has the least vapor pressure, and which forms a constant boiling mixture. Variation in pressure has very little effect on the composition of this constant boiling mixture. Graph #4 shows the boiling points of nitric acids of different concentrations.

From this graph it is evident that 55-60 per cent HNO_3 obtained from absorption systems cannot be concentrated beyond 68-70 per cent HNO_3 by distillation, even fractional distillation. Carpenter and Babor (12) determined that 90 per cent of 20 per cent HNO_3 can be recovered as 55 per cent HNO_3 in three fractionations but to recover 90 per cent of the acid as 65 per cent HNO_3 requires a very considerable number of fractionations. Special methods must be used to obtain the 95 per cent HNO_3 used in the explosives industry, and similar industries where it is necessary to recover the nitrous gases and spent acids in the form of strong HNO_3 .

Many patents have been taken out covering these special methods of concentration. Among the most successful methods used are: distilling the weak HNO_3 with strong H_2SO_4 , the amount of H_2SO_4 used depending upon the initial strength of the dilute HNO_3 ; passing a mixture of H_2SO_4 and HNO_3 down through an acid-proof column up through which a current of steam or hot air is being passed, counter current to the acid mixture. These methods necessitate subsequent concentration of the H_2SO_4 used, so that it may be used over again. It is necessary when using the above methods to have the right pro-

portions of acids present otherwise the methods are not successful. For example, the spent acids from T.N.T. manufacture usually contain 74-75 per cent H_2SO_4 and 5-6 per cent total nitrogen acids, of which only a small part is HNO_3 . Concentrated HNO_3 cannot be obtained from such a mixture by direct distillation. The mixture must be first denitrated by heating and blowing air through it. The NO and NO_2 formed are then recovered as dilute HNO_3 in absorption towers, and then the proper mixture of HNO_3 and H_2SO_4 is made up for concentration by distillation. In the case of the waste acid from nitroglycerin manufacture, the nitrogen acids present in the residue consist mainly of HNO_3 . Their composition is about 75 per cent H_2SO_4 , 8.5 per cent HNO_3 , 14 per cent H_2O , and 2.5 per cent nitroglycerin. From this a certain amount of concentrated HNO_3 can be recovered by direct distillation with steam. Some nitric acid is lost due to reduction of the acid to HNO_2 by organic matter present. The NO evolved must then be recovered in absorption towers.

Other methods are: using arsenic or phosphoric acid as dehydrating agents instead of H_2SO_4 ; mixing liquid NO_2 with HNO_3 ; treating HNO_3 with NO_2 and O_2 under pressure; gassing 70 per cent HNO_3 with NO and O_2 (as N_2O_5) under pressure, and modifications of all the above processes. There are also many other methods patented, which are not commercial as yet. The distillation methods with H_2SO_4 are at present

the cheapest and most commonly used methods.

After the foregoing discussion, in which the principles underlying the absorption and concentration of nitrous gases are explained, it can now be shown that the objectives of the experimental work have an important bearing on the problem of making oxalic acid commercially from corn cobs using nitric acid.

As stated before the process would be cyclic, but neither the nitric acid loss nor cost of recovering the acid could be beyond certain limits for the following reasons. If we assume that one pound of oxalic acid is the maximum yield that can be obtained from a pound of cobs (this is the best yield obtained experimentally so far) and that five pounds of 1.5 HNO_3 must be used to obtain this yield, it is possible to estimate the cost per pound of producing the oxalic acid. The costs will be figured on the basis of ton lots. To treat one ton of cobs requires five tons of 1.5 HNO_3 . The normal first cost of the nitric acid would be about \$110 per ton or \$550 for five tons. After tuning up the cyclic process, the cost of the nitric acid used would be reduced to the cost of recovery plus cost of make-up acid so the cost of producing the oxalic acid should be figured on that basis.

It is hard to arrive at any definite figures in determining the cost of absorbing and concentrating the nitrous gases from this process. Some figures are given in the literature regarding the costs of recovery in other processes but

conditions differ so much between plants that the figures vary between wide limits. The cost of absorption depends mostly on the composition of the gases, as explained previously, while the cost of concentrating depends on the strength of nitric acid recovered from the towers, the cost of H_2SO_4 , and the cost of fuel for the distillation process.

The capital cost of an absorption plant capable of recovering 30 tons of nitric acid (as 100 per cent) per week from gases containing 10-15 per cent NO_2 is given as \$10,000 as an extreme maximum by Webb (10). This would correspond very closely probably to the cost of a layout producing 6 tons of oxalic acid per week by our process. This does not include the cost of the reaction vessels nor the cost of the concentrating plant, but merely the absorption system. In the arc process for the manufacture of HNO_3 , where the hot gases are available for concentration, the capital cost of a concentrating plant is about \$25 per ton of 100 per cent HNO_3 , or for a plant of the above size this would correspond to a capital cost of about \$8000. A plant of the same size for our process would probably cost very much less, although the operating cost would be higher, since the hot arc furnace gases would not be available. The English (15) have adopted a figure of \$15 per ton per annum as the capital cost of a concentrating plant dealing with the dilute HNO_3 from ammonia oxidation processes. The dilute HNO_3 from this process is

about 55 per cent HNO_3 compared with 30 per cent HNO_3 from the arc process. The nitric acid from the oxalic acid process would be recovered as 55-60 per cent HNO_3 , hence, the figure of \$15 per ton is more likely and for a plant of the above size would correspond to about \$4700. No data are available yet regarding the cost of suitable reaction vessels.

The operating costs of an ammonia oxidation process including working of both converter and absorption sections so as to produce a 55 per cent HNO_3 is given by Partington and Parker (13) for English practice as \$10 per ton of HNO_3 (calculated to 100 per cent) in the form of 55 per cent HNO_3 . This includes amortisation at the rate of 10 per cent per annum but does not include interest on capital. Figures obtained from the Muscle Shoals plant in Alabama (14) during a short run after the war give a cost of about \$10 per ton also, so this may be taken as a safe maximum if we assume that the working of the ammonia converter would correspond to working the reaction vessels and working up the mother liquor in the oxalic acid process.

The cost of concentrating 50-55 per cent HNO_3 to 93-96 per cent HNO_3 is given by Webb (10) as \$15 per ton for a minimum cost in American practice. Taylor (15) states that the most probable cost for American practice is from \$20 to \$40 per ton.

If we accept the above figures of \$10 per ton for absorption and \$20 per ton for concentration, the cost of

recovering 5 tons of 1.5 HNO_3 will be \$150. To this must be added the cost of the make-up acid. Average loss of total nitrogen in an absorption system is about 5 per cent, and in a concentrating system is about 3 per cent, making a total loss of about 8 per cent in a recovery system. If an alkaline absorbent is circulated in the last towers of a system the average loss of total nitrogen is 3 per cent. This unrecovered nitrogen is usually in the form of nitric acid mist or unabsorbed NO . Therefore, using the most efficient recovery process, there would be a 6 per cent loss of the total nitric acid used. Of the 5 tons of HNO_3 used at the start, 94 per cent or 4.7 tons will be recovered. At \$110 per ton, the amount of HNO_3 lost per ton of oxalic acid produced will be 6 per cent of \$550 or \$33. Tabulation of estimates give the following figures.

	Amount	Cost
HNO_3 used per ton of oxalic acid produced	5 tons	\$550
HNO_3 recovered as 1.5 HNO_3	<u>4.7 "</u>	<u>517</u>
HNO_3 necessary for make-up	0.3 "	33
Cost of recovering the 4.7 tons HNO_3		<u>150</u>
Total HNO_3 cost per ton of oxalic acid produced		183

The average market price of oxalic acid at present is 11 cents per pound, F.O.B. Works.

Sales price per ton of oxalic acid	\$220
Less cost per ton of oxalic acid (183+10)	193
(assuming cobs at \$10 per ton)	
Gross profit per ton of oxalic acid produced	<u>27</u>

It is believed that the above production cost is a liberal estimate for a well designed plant, but from the gross profit there would have to be deducted interest on capital, cost of packing, etc. Therefore, a plant functioning as above outlined would have to operate within narrow limits between cost of production and income.

Several ways of extending these limits suggest themselves. The first would be to increase the yield of oxalic acid using the same ratio of acid to cob (5:1) as before; a second method would be to obtain the same yield (100 per cent) with a smaller ratio of acid to cob, as 4 to 1 or 3 to 1; another way would be to devise some process whereby the expensive steps of absorption and concentration could be eliminated.

Before anything was done to see if the above objectives could be realized, some experiments were made to secure a nitric acid balance. From a good acid balance it is possible to find out what is happening to the nitric acid used, into what compounds it has been converted, and what treatment it must undergo to be reconverted to the initial stage of 1.5 HNO_3 . Also, it is important to find out if any of the nitric acid is being reduced to N_2O or N_2 , as in these forms the nitrogen is a dead loss and must be added to the 6 per cent mentioned previously. The procedures, data, and results of this investigation are as follows.

The decision was to make several runs in the same manner and using the same type of apparatus as had previously been found to give high yields of oxalic acid. The ratio of 5 parts of 1.5 HNO_3 to 1 part of cobs was used in all the experiments.

Experiment #1.

Object:

To secure a nitric acid balance by determining how much HNO_3 came off as oxides of nitrogen, the amount of each oxide, and the amount of total nitrogen left in the residue in the form of HNO_3 and HNO_2 .

Apparatus:

The set-up was as shown in the figure #1.

A was a 500 cc. Pyrex 3-necked, round bottom flask, B a 500 cc. distilling flask, C a 13-liter aspirating bottle, and D, E, F, G were gas wash bottles.

Procedure:

10 grams of finely ground cobs mixed with 0.1 gram V_2O_5 were placed in flask A. All rubber connections between flasks and bottles were soaked in hot paraffine. After being slipped over the ends of the glass tubing, the paraffine would cool and make air-tight joints. If new connections are used for each run these paraffined rubber connections are quite resistant to cool nitrous oxides. The purpose of flask B was to catch any condensed HNO_3 vapor escaping from the condenser, that of bottle C was to act as a reservoir, both to catch HNO_3 vapor

Figure #1.

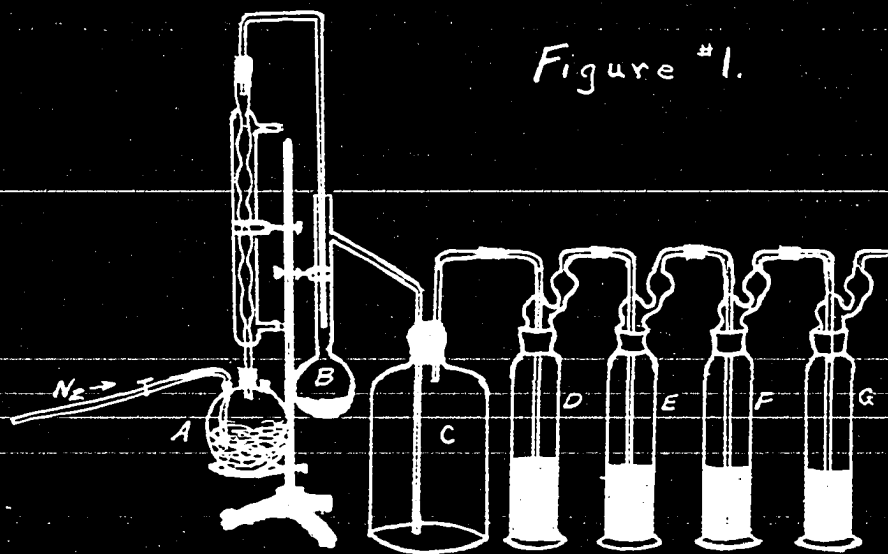
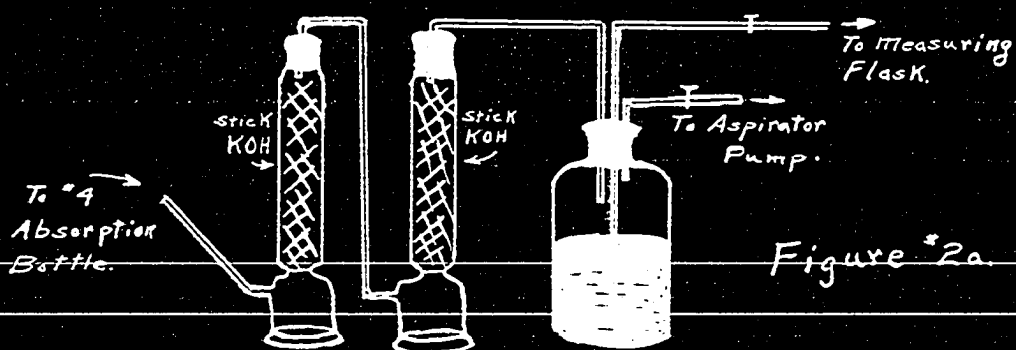
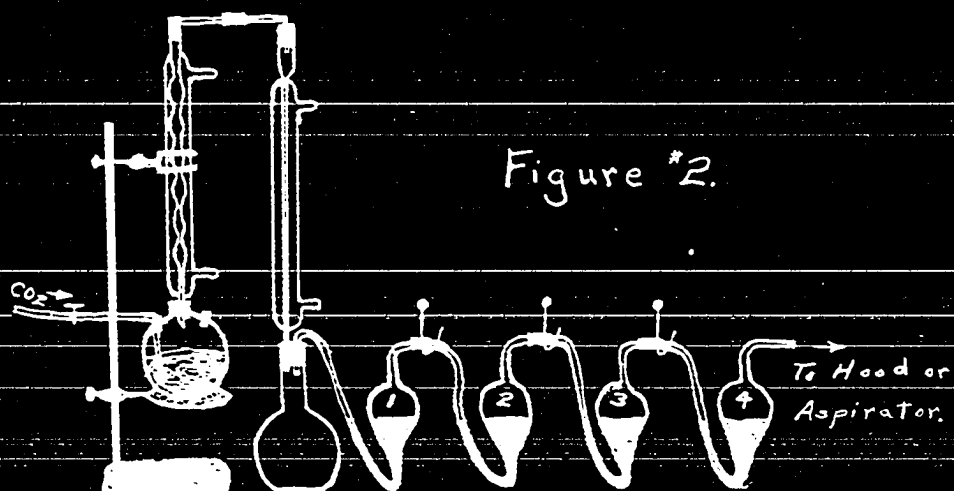


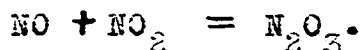
Figure #2.



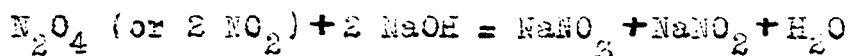
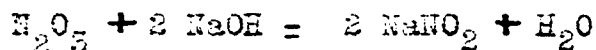
and to prevent the nitrous gases from bubbling too fast through the wash bottles.

Wash bottles D and E each contained 100 cc. of CP. H_2SO_4 (Sp. Gr. 1.84), bottles F and G each contained 100 cc. 1.84 H_2SO_4 to each of which 2 cc. of 1.42 (70 per cent) HNO_3 had been added.

The reason for using strong H_2SO_4 instead of NaOH as an absorbent is as follows. When both NO and NO_2 are present the NO reacts with an equivalent amount of NO_2 to form N_2O_3 .

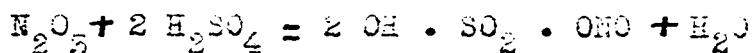
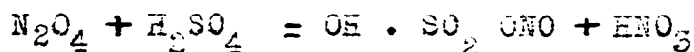


When NaOH is used as an absorbent the reactions are



However, some of the nitrite is oxidized to nitrate at the time of formation causing inaccurate results.

If, as is usually the case, the amount of NO in the gas is less than that required by the peroxide present to form N_2O_3 , the gases can be absorbed rapidly and completely in concentrated H_2SO_4 containing 85-95 per cent H_2SO_4 when the following reactions occur: (10)



If the nitric oxide is in excess of the amount required to form N_2O_3 , this method is inaccurate. However, if

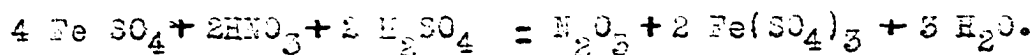
modified by a method suggested by Milligan (16) in which 70 per cent HNO_3 is added in proper amount to concentrated H_2SO_4 in the last absorption bottles of a train the method is accurate regardless of whether or not the NO is in excess of the NO_2 . After a review of the literature this method was chosen as the one most likely to give accurate results.

The nitrosyl sulphuric acid was estimated by titration with K Mn O_4 using Milligan's (16) method for this also. The nitrate nitrogen was determined by the Bowman-Scott ferrous sulphate method. (10). These methods were chosen instead of determining the total nitrogen by the nitrometer, being more convenient and just as accurate. The Bowman-Scott method of determining nitrate nitrogen is as follows:

176.5 grams of ferrous sulphate in 400 cc. of water are stirred into a cooled mixture of 250 cc. of water and 250 cc. of concentrated H_2SO_4 . The whole is cooled and diluted to one liter.

One cc. of this solution is equivalent to 0.02 grams HNO_3 and contains 0.8 cc. of water. It is standardized by titration with 1 N HNO_3 , standardized with alkali. To 100 cc. H_2SO_4 , 10 cc. of 1 N HNO_3 are added with a pipette. The ferrous sulphate solution is then run in from a burette until a pinkish brown color appears. After a little practice, this color is very easy to identify. The color is due to the fact that when an excess of ferrous iron is present it combines with the reduced nitrogen compounds to form a red com-

pound. The reaction is



The titration must be carried out in a concentrated H_2SO_4 solution, the H_2SO_4 content of which must not fall below 75 per cent at the end of the reaction.

Under these conditions, provided that the temperature is not allowed to exceed 60°C , nitric acid is not reduced to NO , but only to N_2O_3 . Consequently nitrous acid does not interfere. Results accurate to 1 in 300 can readily be obtained. The titration is best carried out by putting the beaker in a white porcelain evaporating dish containing cold water. The end point color shows up readily against the white dish. After standardizing, unknowns are determined by substituting 10 cc. of unknown in 100 cc. of concentrated H_2SO_4 .

After the apparatus was set up, nitrogen was passed through the system for one hour. Then 35 cc. of 1.5 HNO_3 and the catalyst (V_2O_5) were added to the cobs through the separatory funnel. The nitrogen was then shut off, and the reaction was allowed to proceed without being heated or cooled until the second vigorous reaction set in. The purpose of the nitrogen was to clean all oxygen out of the system so that no NO would go to NO_2 . When the catalytic reaction had started the flask was cooled with tap water for 16 hours. The nitrous gases collected in the top of A, in B, and in C. After the reaction had subsided, a moderate stream of nitrogen was passed through the system. The stream of nitrogen was maintained

through the system for 18 hours. For the first 16 hours the rate was 2 bubbles per second. For the last two hours it was somewhat faster. By this time the system seemed entirely clear of brown fumes, and a good yield of crystals remained in flask A. No brown fumes progressed beyond bottle B, and none were seen to issue from the last bottle (G) at any time.

After 18 hours the contents of the wash bottles were analyzed for NO and NO₂. A slight amount of condensate in B and C was analyzed for HNO₃ and HNO₂. The residue in flask A was analyzed for HNO₃, HNO₂, and oxalic acid.

Methods used in the analysis:

For nitrosyl sulphuric in wash bottles - KMnO₄ titration.

For nitrate nitrogen " " " - ferrous sulphate.
(Bowman-Scott method)

For HNO₂ in B and C - KMnO₄ titration.

For HNO₂ " " " " - Bowman-Scott method.

For HNO₃ in residue - Bowman-Scott method.

For HNO₂ in residue - KMnO₄ titration.

For (COOH)₂.2H₂O in residue - precipitation with CaCl₂, then titration with KMnO₄.

Total acidity - titration with NaOH using phenolphthalein as an indicator.

The data and calculations for the analyses for this experiment will be given in detail. In the succeeding experiments, to conserve time and space, only the data and results will be given, except when some change was made necessitating explanation.

analysis of absorbent in wash bottles D and E.

The 200 cc. of absorbent in wash bottles D and E were made up to 500 cc. with 1.84 H_2SO_4 .

1 cc. of the FeSO_4 solution was equivalent to 0.021 grams HNO_3 or 0.00467 grams Nitrogen.

The KMnO_4 solution was 0.10 N

9.8 cc. FeSO_4 = 10 cc. of absorbent acid.

50 cc. KMnO_4 = 10 cc. of absorbent acid.

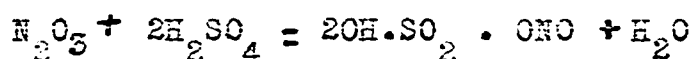
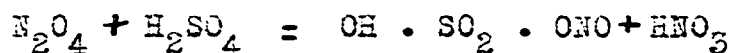
1 cc. 0.10 N KMnO_4 = 0.0014 grams nitrogen

Then:

Nitrogen (in 500 cc. of solution) as nitrate nitrogen =
2.288 grams.

Nitrogen (in 500 cc. of solution) as nitrosyl nitrogen =
3.50 grams.

Knowing these two figures, from the reactions



the amounts of N_2O_3 and NO_2 (N_2O_4) can be calculated.

$$3.50 - 2.288 = 1.212 \text{ gms. N}_2 \text{ as N}_2\text{O}_3$$

$$\text{and } 2(2.288) = 4.576 \text{ gms. N}_2 \text{ as NO}_2 \text{ (N}_2\text{O}_4)$$

$$4.576 \text{ grams N}_2 \text{ as NO}_2 = 15.035 \text{ grams NO}_2$$

$$1.212 \text{ grams N}_2 \text{ as N}_2\text{O}_3 = 1.991 \text{ grams NO}_2$$

and 1.299 grams NO

$$15.035 + 1.991 = 17.026 \text{ gms. NO}_2 = 23.32 \text{ grams HNO}_3$$

$$1.299 \text{ gms. NO} = 2.727 \text{ grams HNO}_3$$

Total HNO_3 from bottles D and E = 26.047 grams.

Data for wash bottles F and G.

The 200 cc. of absorbent in bottles F and G were also made up to 500 cc. with $1.84 \text{ H}_2\text{SO}_4$.

$21.6 \text{ cc. FeSO}_4 = 50 \text{ cc. of absorbent acid.}$

$9.5 \text{ cc. } 0.10 \text{ N KmnO}_4 = 50 \text{ cc. of absorbent acid.}$

However 4 cc. of 1.42 HNO_3 (70 per cent) had been added to the H_2SO_4 in these bottles, and had to be corrected for.

$1 \text{ cc. } 1.42 \text{ HNO}_3 = 47.3 \text{ cc. FeSO}_4$

$4 \text{ cc. } 1.42 \text{ HNO}_3 = 189.2 \text{ cc. FeSO}_4$

$216 - 189.2 = 26.8 \text{ cc. FeSO}_4 = 500 \text{ cc. of absorbent acid.}$

Then

Nitrogen (in 500 cc. of solution) as nitrate nitrogen =
0.125 grams.

Nitrogen (in 500 cc. of solution) as nitrosyl nitrogen =
0.133 grams.

Calculating in the same manner as before, one obtains:

Total HNO_3 from bottles F and G = 1.157 grams.

Total HNO_3 from bottles D, E, F, and G = 27.2 grams.

Total NO_2 was 17.026 0.6322 = 17.658 grams.

Total NO was 1.299 0.006 = 1.307 grams.

Considering only the nitrogen oxides absorbed we obtain the following per cents by volume:

$\text{NO}_2 = 90 \text{ per cent}$

$\text{NO} = 10 \text{ per cent}$

Analysis of Condensate in flasks B and C:

The slight amount of condensate in flasks B and C was made up to 200 cc. with water.

Total acidity:

24.1 cc. of 0.08577 N NaOH = 10 cc. of the 200 cc.

Normality of condensate = 0.2017 N

Nitrogen acid present as HNO_3 :

5.6 cc. FeSO_4 = 10 cc. of the 200 cc.

112 cc. FeSO_4 = 200 cc. of the 200 cc. = 2.552 grams HNO_3 .

Nitrogen acid present as HNO_2

1.1 cc. 0.1 N KMnO_4 = 10 cc. of the 200 cc.

22 cc. N KMnO_4 = 200 cc. of the 200 cc. = 0.1034 grams HNO_2

0.1034 grams HNO_2 = 0.1386 grams HNO_3

Total HNO_3 = 2.352 + 0.1386 = 2.4906 grams.

2.4906 grams HNO_3 per 200 cc. = 0.2N solution

which agrees very well with the normality derived from the total acidity.

Analysis of Residue in flask A.

The residue in flask A consisted of mother liquor, crystals of oxalic acid, and a small amount of pulped cob particles. Distilled water (about 600 cc.) was added to the contents. Then the flask was gently heated until the oxalic acid crystals were dissolved. The solution was then filtered and after cooling, it was made up to 1000 cc. with distilled water. The oxalic acid was determined by making an aliquot part ammoniacal, then precipitating with CaCl_2 , then dissolving with H_2SO_4 , followed by titration with KMnO_4 .

Oxalic Acid determination:

12 cc. 0.1 N KMnO_4 = 10 cc. of the 1000 cc.

1200 cc. 0.1 N KMnO_4 = 1000 cc. = 7.56 grams $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$

Since 10 grams of cobs were used the yield of oxalic acid was 75.6 per cent on an air dry basis.

Total acidity:

31.3 cc. 0.08577 N NaOH = 10 cc. of the 1000 cc.

Normality of solution = 0.2622

The amount of nitrogen acids was determined in two ways to obtain a check if possible. Using the above figures the normality due to the oxalic acid was subtracted from the total normality.

7.56 63 = 0.12 N in oxalic acid.

0.2622 - 0.12 = 0.1422 N due to the nitrogen acids.

If one considers all of this normality as due to HNO_3 and none to HNO_2 or other acids, the amount of HNO_3 present was 8.96 grams.

0.1422 x 63 = 8.96 grams.

Then the contents were analyzed for both HNO_3 and HNO_2 , using the Bowman-Scott ferrous sulfate method for the HNO_3 , and Milligan's modified KMnO_4 method for the HNO_2 with these results:

2.3 cc. FeSO_4 = 10 cc. of 1000 cc.

230 cc. FeSO_4 = 1000 cc. = 4.85 grams HNO_3

(The presence of oxalic acid does not interfere with this method of determining HNO_3).

15.8 cc. 0.1 N KMnO_4 = 10 cc. of the 1000 cc.

Correcting for the oxalic acid present.

15.8 - 12 = 3.8 cc. 0.1 N KMnO_4 = 10 cc. of the 1000 cc.

or 580 cc. of .1 N KMnO_4 = 1000 cc. = 1.786 grams HNO_2 or
2.181 grams HNO_3

Total HNO_3 by this method:

$$4.83 + 2.181 = 6.99 \text{ grams } \text{HNO}_3$$

This compares with 8.96 grams obtained from the first method. This difference was probably due to other possible organic acids present. If we assume that 6.99 grams was the correct value the results of the experiment were as follows:

HNO_3 accounted for:

In absorbent	27.20	grams
As condensate	2.49	"
In mother liquor	<u>6.99</u>	"
Total	36.68	"

HNO_3 used: (33 cc. of 1.5 HNO_3 were used)

$$66.5 \text{ cc. } \text{FeSO}_4 = 1 \text{ cc. of } 1.5 \text{ } \text{HNO}_3$$

$$12.1 \text{ cc. } 0.1 \text{ N } \text{KMnO}_4 = 10 \text{ cc. of } 1.5 \text{ } \text{HNO}_3$$

HNO_3 as HNO_3

$$66.5 (33) (0.021) = 46.08 \text{ grams.}$$

HNO_3 as HNO_2

$$1.21 (33) (0.0065) = 0.252 \text{ grams}$$

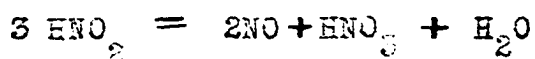
$$\text{Total } \text{HNO}_3 \text{ used} = 46.08 + 0.252 = 46.33 \text{ grams as } 100\% \text{ } \text{HNO}_3.$$

Per cent recovery and accounted for:

$$(36.68 / 46.33) \times 100 = 79.1 \text{ per cent.}$$

This was a rather low recovery. Two probable ways of accounting for the lost HNO_3 are: some of the HNO_3 may have been combined with the pulped cobs, remaining in the residue,

in the form of a nitrated compound for which no analysis was made; secondly, when water was added to the contents of the flask a brisk evolution of gas took place. This may have been due to the reaction.



which takes place when concentrated solutions of HNO_2 are diluted with water. The gas evolved was not recovered and may have been NO as shown by the above equation. In the succeeding experiments this gas was recovered, and while it affected the results showing the percentages of NO_2 and NO in the gases evolved during the reaction, a better accounting for HNO_3 used was obtained.

Experiment #2.

The object of this experiment was to find out how efficient the gas wash bottles were as absorbing vessels, and to ascertain how many were needed in the absorption train.

The materials and set-up were the same as in experiment #1, except 100 cc. of 1.84 H_2SO_4 were placed in each of bottles D and E, while bottle F held 50 cc. of 0.136 N KMnO_4 and bottle D contained 25 cc. 0.8377 N NaOH colored with phenolphthalein.

Procedure:

Nitrogen was run through the system for thirty minutes, then the 1.5 HNO_3 was added, and the reaction allowed to proceed until the second vigorous reaction had started. At this point the flask was cooled. Then a water aspirator attached

to the outlet end of the system was started and run for thirty minutes. Next a stream of nitrogen was passed through the system for 15 minutes. Then water was added to the contents of the flask and nitrogen was passed through until the system was clear of brown fumes.

The NaOH solution was bleached clear soon after the second reaction had subsided. The KMnO_4 solution turned clear near the end of the run, at which time the system was about clear of brown fumes.

Since the NaOH and KMnO_4 solutions were both bleached out, evidently absorption was not complete. It was thought that under the circumstances no accurate balance could be obtained so no analyses of the contents of the gas wash bottles were made.

Experiment #3.

The object of this experiment was to secure a better HNO_3 balance than had been obtained in Experiment #1.

The materials and set-up were the same as in Experiment #1. Wash bottles D and E, each contained 100 cc. 1.84 H_2SO_4 ; bottles F and G each held 100 cc. of 1.84 H_2SO_4 , each 100 cc. containing 2 cc. of 1.42 HNO_3 . Another bottle H was added to the system. It contained 60 cc. H_2SO_4 and 2 cc. of 1.42 HNO_3 .

Procedure:

Nitrogen was passed through the system for one hour. Then the 1.5 HNO_3 was added, and the reaction allowed to pro-

ceed until the catalytic reaction had started. The flask was then cooled. Two liters of unabsorbed gas had come off up to this stage, but as no brown fumes had passed beyond wash bottle E, it is believed this gas was a mixture of nitrogen and carbon dioxide.

The aspirator pump was started, and the fumes from the reaction flask were slowly drawn off for 24 hours. Then water was added to the residue consisting of mother liquor and oxalic acid crystals, and the pumping was maintained until evolution of gas had subsided. Nitrogen was then passed through for thirty minutes, after which the contents of the respective vessels were analyzed in a manner similar to that of Experiment #1.

Results:

HNO_3 accounted for:

In absorbents	40.670	grams
As condensate and mother liquor..	7.407	"
Total	47.077	"

HNO_3 used = 46.33 grams (as 100 per cent HNO_3).

Per cent recovery and accounted for:

$(47.077 \div 46.33) \times 100 = 102$ per cent.

Nitrogen oxides absorbed:

Per cent NO_2 by volume = 91.03

Per cent NO by volume = 8.97

Yield of oxalic acid = 5.14 grams.

Since 10 grams of cobs were used, the yield of oxalic acid was

51.4 per cent on an air dry basis.

As shown above more acid was recovered than was used. The error probably arose in the analyses of the gases as the per cent of HNO_3 absorbed as gases seems too high with respect to the HNO_3 remaining in the mother liquor. A recheck of calculations failed to locate the source of error. The FeSO_4 solution was standardized each day it was used.

Data and Calculations:

The absorbent acids from the various wash bottles were lumped together and made up to 1000 cc. with 1.84 H_2SO_4 . 8.1 cc. FeSO_4 = 10 cc. of the 1000 cc. (after correcting for the HNO_3 present).

1 cc. FeSO_4 = 0.00458 grams nitrogen.

810 (0.00458) = 3.71 grams N_2 as nitrate nitrogen.

38.16 cc. 0.1 N KMnO_4 = 10 cc. of the 1000 cc.

1 cc. 0.1 N KMnO_4 = .0014 grams nitrogen.

3816 (.0014) = 5.34 grams N_2 as nitrosyl nitrogen.

5.34 - 3.71 = 1.63 grams N_2 as N_2O_3

2(3.71) = 7.42 grams N_2 as NO_2

7.42 gms. N_2 as NO_2 = 24.4 gms. NO_2 = 35.35 gms. HNO_3 .

1.63 gms. N_2 as N_2O_3 = 2.675 gms. NO_2 = 3.66 gms. HNO_3
= 1.745 gms. NO = 3.66 gms. HNO_3

Total HNO_3 = 40.67 grams.

Total NO_2 = 27.075 gms.

Total NO = 1.745 gms.

$$27.075 \times 22.4 \div 46 = 13.2$$

$$1.745 \times 22.4 \div 30 = \underline{1.3}$$

$$14.5$$

$$(13.2 \div 14.5) \ 100 = 91.03 \text{ per cent } \text{HNO}_2 \text{ by volume.}$$

$$(1.3 \div 14.5) \ 100 = 8.97 \text{ per cent } \text{HNO}_2 \text{ by volume.}$$

The contents of the reaction vessel were dissolved, filtered, and made up to 1000 cc.

Oxalic acid determination:

$$6 \text{ cc. of } 0.136 \text{ N } \text{KMnO}_4 = 10 \text{ cc. of the 1000 cc.}$$

HNO_3 determination: (of HNO_3 as HNO_2).

$$3.2 \text{ cc. } \text{FeSO}_4 = 10 \text{ cc. of the 1000 cc.}$$

$$1 \text{ cc. } \text{FeSO}_4 = 0.02058 \text{ grams } \text{HNO}_2.$$

HNO_3 determination: (of HNO_3 as HNO_2)

$$5.3 \text{ cc. } 0.136 \text{ N } \text{KMnO}_4 = 10 \text{ cc. of the 1000 cc. (after correcting for the oxalic acid present).}$$

$$1 \text{ cc. } 0.136 \text{ N } \text{KMnO}_4 = 0.008568 \text{ grams } \text{HNO}_3$$

$$\text{Total } \text{HNO}_3 = 7.407 \text{ grams.}$$

Total Acidity:

$$62 \text{ cc. of } 0.041885 \text{ N } \text{NaOH} = 10 \text{ cc. of the 1000 cc.}$$

$$\text{Normality of solution} = 0.2597$$

$$\text{Normality due to oxalic acid} = \underline{0.0816}$$

$$\text{Normality due to other acids} = 0.1781$$

If we assume this normality is due entirely to HNO_3 ,
then

$$0.1781 \times 63 = 11.2 \text{ grams } \text{HNO}_3 \text{ remained in the mother liquor. This result compared with 7.407 grams obtained above}$$

would give a larger error. It is probable that other organic acids besides oxalic were present in small amounts.

Experiment #4:

The object of this experiment was to secure a better HNO_3 balance. The set-up shown in the sketch #2 was used in order to secure better absorption. The absorbing flasks were 100 cc. pipettes filled with short pieces of solid glass rod, and then the tubing on the ends was bent over as shown in the sketch #2.

Materials:

10 grams ground cobs, 0.1 gram V_2O_5 , and 33 cc. 1.5 HNO_3 .

Procedure:

The apparatus was set up. Then the cobs and catalyst were placed in the flask and carbon dioxide was passed slowly through the system for one hour. Next, the 1.5 HNO_3 was added and the reaction was allowed to proceed until the catalytic reaction set in. The flask was then cooled. An aspirator pump was started so that the absorbent would not be pulled out of the absorbing pipettes. After cooling the flask, the contents were drenched by adding water through a separatory funnel. Then a stream of CO_2 gas was passed through the system for two hours. The system was clear of brown fumes long before the two hours had elapsed. The contents of the respective flasks were then analyzed. The pur-

pose of drenching the contents of the reaction flask at once, was to prevent the formation of oxalic acid so that there would be no interference with the determination of HNO_2 . No brown fumes were seen beyond the third absorption flask.

Data and Calculations:

Absorption flasks #1 and #2 each contained 25 cc. of 1.84 H_2SO_4 . #3 and #4 each contained 25 cc. 1.84 H_2SO_4 and 2 cc. 1.42 HNO_3 as suggested by Milligan (16). After the run was completed, the absorbent acids from all the flasks were lumped together. The flasks were washed twice with 1.84 H_2SO_4 and the washings added to the rest of the absorbent, which was then made up to 250 cc. with 1.84 H_2SO_4 .

33.6 cc. FeSO_4 = 10 cc. of the 250 cc.

1 cc. FeSO_4 = 0.004547 grams nitrogen

(standardized against 1.02 N HNO_3)

33.6 (25) = 840 cc. FeSO_4 = 250 cc. of the absorbent.

Correcting for the HNO_3 initially present.

840 - 4(48.54) = 643.84

643.84(0.004547) = 2.93 grams N_2 as nitrate nitrogen.

75.3 cc. 0.136 N KMnO_4 = 10 cc. of the 250 cc.

1cc. 0.136 N KMnO_4 = 0.001904 gram nitrogen.

75.3(25) (0.001904) = 3.59 grams N_2 as nitrosyl nitrogen.

3.59 - 2.93 = 0.66 grams N_2 as N_2O_3

2(2.93) = 5.86 grams N_2 as NO_2

5.86 grams N_2 as NO_2 = 19.2 grams NO_2 = 26.35 grams HNO_3 .

$$0.66 \text{ grams } N_2 \text{ as } N_2O_3 = \begin{cases} 1.084 \text{ grams } NO_2 = 1.485 \text{ grams } HNO_3 \\ 0.705 \text{ grams } NO = \underline{1.485} \text{ grams } HNO_3 \end{cases}$$

Total 29.320 grams HNO_3 .

Total NO_2 = 20.284 grams = 94.96 per cent by volume.

Total NO = 0.705 grams = 5.04 per cent by volume.

The residue in the reaction flask was filtered and made up to 1000 cc. with water.

10.9 cc. $FeSO_4$ = 10 cc. of the 1000 cc.

1 cc. $FeSO_4$ = 0.01265 cc. HNO_3

1090(0.01265) = 13.79 grams HNO_3 as HNO_3 .

4.9 cc. of 0.166 N $KMnO_4$ = 10 cc. of the 1000 cc.

1 cc. of 0.166 N $KMnO_4$ = 0.01045 grams HNO_3

490 (0.01045) = 5.12 grams HNO_3 as HNO_2

Total HNO_3 recovered and accounted for:

In absorbent 29.32

In reaction flask 18.91

Total 48.23 grams HNO_3

HNO_3 used (53 cc.) = 48.557 (as 100 per cent HNO_3).

71.5(53)(0.02046) = 48.275 grams as HNO_3

1(53)(0.008544) = 0.282 grams as HNO_2

Total 48.557

(A fresh stock of 1.5 HNO_3 was used for this experiment).

Per cent HNO_3 accounted for:

(48.23 ÷ 48.557) 100 = 99.4 per cent.

Note: The $FeSO_4$ and $KMnO_4$ used in titrating the 1.5 HNO_3 were

new solutions and differed in strength from the solutions used in analyzing the contents of the absorption flasks and reaction vessel.

A qualitative test for oxalic acid gave a negative result.

Experiment #5.

The object of this experiment was to secure a nitric acid balance.

Materials:

10 grams ground cobs, 0.1 gram V_2O_5 , 55 cc. of 1.5 HNO_3 .

Procedure:

The procedure for this experiment was the same as for Experiment #4, and the set-up was also the same. The only exception was that the contents of the reaction vessel, after the addition of water, were allowed to stand for 24 hours. During this 24 hours, an aspirator pump, attached to the exit end of the system, slowly pulled into the absorbent any gases evolved from the reaction flask.

Data and Calculations:

The absorbent acids plus washings were made up to 250 cc. with 1.84 H_2SO_4 .

72.9 cc. $FeSO_4$ = 10 cc. of the 250 cc.

1 cc. $FeSO_4$ = 0.00277 gram nitrogen.

72.9 (25) = 1822.5 cc. = 250 cc. of the 250 cc.

Correcting for the 1.42 HNO_3 initially present.

$$1822.5 - 6(86.6) = 1302.9 \text{ cc.}$$

$$1302.9 (0.00277) = 3.61 \text{ grams } \text{N}_2 \text{ as nitrate nitrogen.}$$

$$94.5 \text{ cc. } 0.156 \text{ N } \text{KMnO}_4 = 10 \text{ cc. of the 250 cc.}$$

$$1 \text{ cc. } \text{N } \text{KMnO}_4 = 0.001904 \text{ gram nitrogen.}$$

$$94.5(25)(0.001904) = 4.5 \text{ grams } \text{N}_2 \text{ as nitrosyl nitrogen.}$$

$$4.5 - 3.61 = 0.89 \text{ grams } \text{N}_2 \text{ as } \text{N}_2\text{O}_3$$

$$2(3.61) = 7.22 \text{ grams } \text{N}_2 \text{ as } \text{NO}_2$$

$$7.22 \text{ grams } \text{N}_2 \text{ as } \text{NO}_2 = 23.72 \text{ grams } \text{NO}_2 = 32.5 \text{ grams } \text{HNO}_3$$

$$2.925 \text{ grams } \text{NO}_2 = 4.0 \text{ grams } \text{HNO}_3$$

$$0.89 \text{ grams } \text{N}_2 \text{ as } \text{N}_2\text{O}_3 =$$

$$1.905 \text{ grams } \text{NO} = \underline{4.0 \text{ grams } \text{HNO}_3}$$

$$\text{Total} \quad 40.5 \text{ grams } \text{HNO}_3$$

$$\text{Total } \text{NO}_2 = 26.645 \text{ grams} = 90.1 \text{ per cent by volume}$$

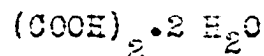
$$\text{Total } \text{NO} = 1.905 \text{ grams} = 9.9 \text{ per cent by volume}$$

The liquor in the reaction flask was filtered and made up to 1000 cc. with water.

Oxalic acid determination:

$$15 \text{ cc. } 0.166 \text{ N } \text{KMnO}_4 = 100 \text{ cc. of the 1000 cc.}$$

$$150 \text{ cc. } 0.166 \text{ N } \text{KMnO}_4 = 1000 \text{ cc.} = 1.569 \text{ grams}$$



$$\text{Yield of oxalic acid} = 15.69 \text{ per cent}$$

HNO_3 determination:

$$2.4 \text{ cc. } \text{FeSO}_4 = 10 \text{ cc. of the 1000 cc.}$$

$$1 \text{ cc. } \text{FeSO}_4 = 0.01264 \text{ gram } \text{HNO}_3$$

$$240(0.01265) = 3.04 \text{ HNO}_3 \text{ as HNO}_3.$$

HNO₂ determination:

5cc. KMnO₄ = 10 cc. of the 1000 (after correcting for oxalic).

$$1 \text{ cc. } 0.166 \text{ N KMnO}_4 = 0.01045 \text{ gram HNO}_3.$$

$$500 (0.01045) = 5.23 \text{ grams HNO}_3 \text{ as HNO}_2.$$

Total Acidity:

$$44 \text{ cc. } 0.041885 \text{ N NaOH} = 10 \text{ cc. of the 1000 cc.}$$

$$\text{Normality of Solution} = 0.1841$$

Total HNO₃ recovered and accounted for:

In absorbent 40.5 grams

In reaction flask 8.27 grams

Total 48.77 grams

$$\text{HNO}_3 \text{ used (33 cc.)} = 48.557 \text{ grams (as 100 per cent HNO}_3)$$

Per cent HNO₃ accounted for:

$$(48.77 \div 48.557)100 = 100.4 \text{ per cent}$$

Results of the four experiments:

No.	Volume per cent NO ₂	of oxides NO	HNO ₃ accounted for	Per cent Recovery
#1	90	10	36.68 grams	79.1
#3	91.03	8.97	47.077 grams	102
#4	94.96	5.04	48.23 grams	99.4
#5	90.1	9.9	48.77 grams	100.4

As stated previously, the purpose of securing a nitric acid balance, i. e., to account for all the nitric acid used, was to ascertain if any of the HNO₂ was being reduced to

N_2O or N_2 . It is believed that the methods used in analyzing the absorbing liquid for NO_2 and NO are sufficiently accurate but there is some uncertainty regarding the accuracy of the methods used in analyzing the contents of the reaction flask for HNO_3 and HNO_2 , although the methods used seemed the most suitable ones. However, it seems likely that some of the HNO_3 ought to be combined with the pulped cob residue as a nitro-cellulose compound or some other nitrated organic compound, and any HNO_3 in this form would not be determined by the above method.

To get around this difficulty another experiment was made, the object of which was to absorb all CO_2 , NO_2 , and NO , and examine any residual gas for N_2O and N_2 . Since N_2O , NO and NO_2 are all soluble in water and alkali solutions, these cannot be used as absorbents. Webb (10) recommends using moist stick potash for removing CO_2 , NO , and NO_2 and estimating any nitrous oxide in the residual gas by solution in water in a suitable gas burette. Instead of using moist stick potash to remove CO_2 , NO , and NO_2 , the NO and NO_2 were removed with 1.84 H_2SO_4 (in which N_2O is insoluble), and the CO_2 was removed with moist stick potash. This method offered a better opportunity to analyze the gases for NO and NO_2 .

Experiment #6.

The object of this experiment was to determine if any N_2O or N_2 was evolved during the reaction.

Materials:

10 grams of ground cobs, 0.1 gram V_2O_5 , 33 cc. of
1.5 HNO_3 .

Apparatus:

The apparatus is shown in figure #2a. The flasks containing 1.84 H_2SO_4 were to absorb the NO_2 and NO , the CO_2 towers filled with moist stick potash were to catch the CO_2 , and the aspirator bottle was to act as a receiver for N_2O , N_2 or other residual gases.

Procedure:

The cobs and catalyst were placed in the reaction flask, CO_2 was passed through the system for 2 hours at a slow rate and with the CO_2 towers cut out. Then the CO_2 towers were joined to the system and CO_2 passed through them for 10 minutes. The 1.5 HNO_3 was added to the cobs, and the outlet cock from the aspirator bottle was opened. There was a momentary flow of water from the aspirator bottle, but after a few cubic centimeters had dropped there was no further flow. The water in the aspirator bottle was covered with a layer of liquid paraffine to prevent any N_2O from being dissolved in it. Absorption seemed to be complete during the reaction as no water flowed from the aspirator bottle. However, when the catalytic reaction set in and the reaction flask was cooled, it was necessary to start the aspirator pump to prevent a back flow in the system. For this reason

another run was made, identical with the first and with similar results, except when the catalytic reaction set in, the flask was not cooled, but the reaction was allowed to go to completion. During the second reaction water began to flow from the aspirator bottle and about a liter came off. When the second reaction subsided, the reaction flask began to cool and it was necessary to start the aspirator pump to prevent back flow. The pump drew the residual gas out of the aspirator bottle so no analysis of the residual gas was possible. It is believed that it consisted of CO_2 evolved so rapidly that the moist stick potash was unable to absorb it.

Analysis of the H_2SO_4 absorbent and of the contents of the reaction flask gave the following results:

Total HNO_3 recovered and accounted for:

In absorbent 26.00 grams

In reaction flask 20.44 grams

Total 46.44 grams

HNO_3 used = 46.557 grams (as 100 per cent HNO_3).

Per cent HNO_3 accounted for:

$(46.44 \div 46.557) 100 = 95.5$ per cent.

Composition of nitrous oxide gases.

$\text{NO}_2 = 82.3$ per cent by volume.

$\text{NO} = 17.7$ per cent by volume.

No further work was done to ascertain if any N_2O was formed during the reaction. From the high percentage of NO_2

present it seems probable that no reduction to N_2O or N_2 takes place.

Webb (10) states that N_2O , along with NO_2 and NO , is evolved when organic matter is oxidized by nitric acid, but is usually present to the extent of less than 0.5 per cent by volume.

Cottrell (11) states that starch decomposes nitric acid with production of NO , NO_2 , and N_2O_5 .

The object of the next series of experiments was to ascertain if the expensive processes of absorption and concentration of the nitrous oxides could either be eliminated or else be modified so as to be less costly.

The first investigation pertained to the effect of the evolved nitrous gases on cobs. In other words, the cobs were pretreated with nitrous oxides to find out if this pretreatment would decrease the amount of 1.5 HNO_3 required per pound of cobs, or conversely, to ascertain if an increased yield of oxalic acid would result using the 5 to 1 ratio.

Experiment #1.

The apparatus is shown in figure #3. 20 grams of ground cobs and 0.2 gram V_2O_5 were placed in flask B, and a like quantity in flask C. Flask A contained 125 grams As_4O_6 (lump), 160 grams 1.5 HNO_3 , and 75 grams of 1.84 H_2SO_4 to make $NO_2(N_2O_4)$ according to Cundall's method (10).

The reaction is:

Figure #3.

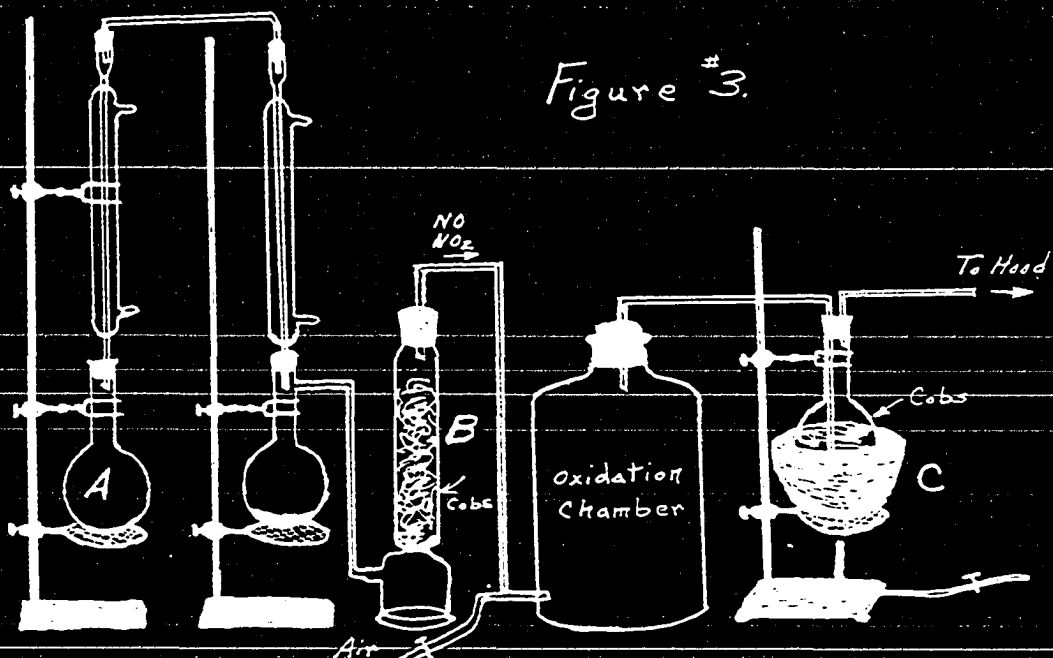


Figure #4.

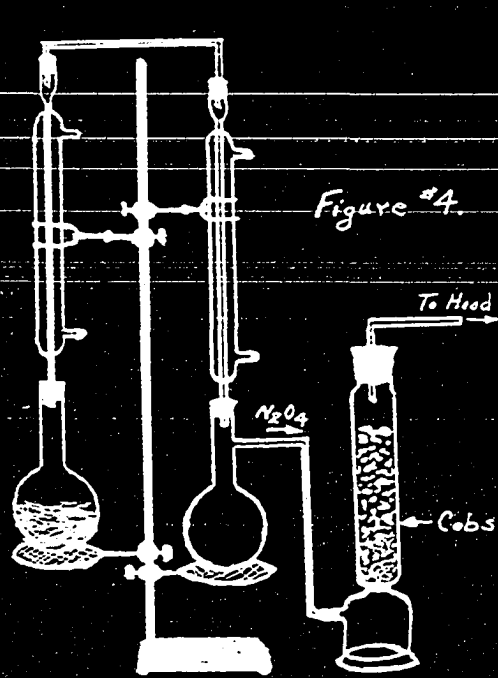
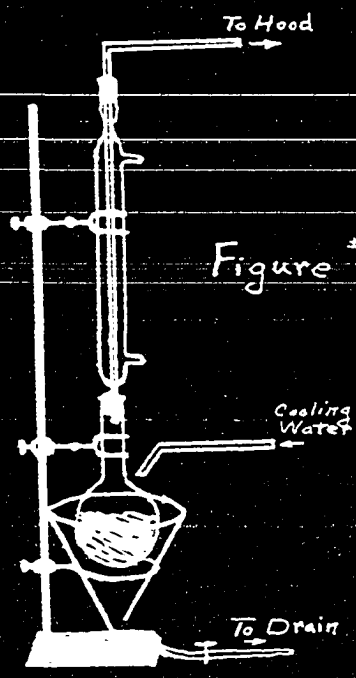
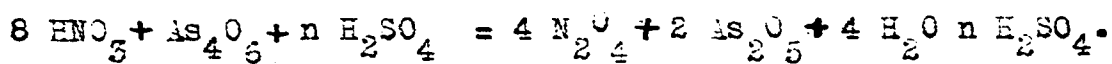


Figure #5.





The N_2O_4 was cooled in a straight condenser, then passed into B at about 40°C . The fumes from B were mixed with air and then passed into C. From C the fumes were vented to a hood. Flask C was kept at 80°C with an oil bath. A strong stream of N_2O_4 was passed through B and C for 8 hours. The contents of B and C were stirred at intervals with a glass rod. The mixture in flask A had to be renewed at intervals of about 3 hours.

Observations:

If the hot gases from A are not cooled the cobs in B catch fire, (at a temperature of about 90°C).

When the hot gases are cooled to 40°C , the reaction of the gases on the cobs barely warms the flask.

The contents of flask C caught fire when the temperature of the oil bath rose to 92°C . A new charge of cobs was then substituted.

Results:

The cobs in both B and C were stained a light yellow color, were softened slightly, and were a trifle damp. Otherwise they seemed to be unchanged.

Experiments 2, 3, 4, 5 and 6.

In this series, the set-up shown in Figure #4 was used for pretreating the cobs with N_2O_4 , then the set-up shown in Figure #5 was used for treating the cobs with 1.5 HNO_3 .

Procedure:

20 grams of ground cobs were treated for various intervals with N_2O_4 . Then the treated cobs were mixed with 1.5 HNO_3 in varying amounts in the presence of 0.2 gram V_2O_5 . Observations and results of these five runs are tabulated below. The time of treatment with N_2O_4 fumes, and the amount of 1.5 HNO_3 used are also given.

Number	Remarks	Results
#2	NO_2 treatment - 1 hour Added 80 grams 1.5 HNO_3 but did not heat. Cooled at start of catalytic reaction.	Cobs slightly pulped. Catalytic reaction seem to be delayed. After 48 hours, a pulpy greenish yellow residue remained. No crystals present.
#3	Same as #2 except 100 grams 1.5 HNO_3 were added.	Cobs caught fire and batch was ruined.
#4	Same as #3.	Cobs also caught fire.
#5	NO_2 treatment - 3 hours, then let stand overnight in NO_2 fumes. Added 100 grams 1.5 HNO_3 .	Cobs slightly pulped, and damp. Cobs slowly decomposed. Catalytic reaction extremely moderate. Good yield of crystals. Yield = 65%.
#6	N_2O_3 treatment - 1 hour (The N_2O_3 was generated by As_4O_6 4 HNO_3 = 4 H AsO_3 2 N_2O_3 using same set-up as for N_2O_4). Added 100 grams 1.5 HNO_3 .	The reaction was the same as if no pretreat- ment had been made. Yield = 81.5%

In the next five experiments, the cobs were pretreated with fumes evolved from a large batch of cobs mixed with

$38^{\circ}\text{Be HNO}_3$ (57%). The set-up was the same as that shown in Figure #4, except the flask containing cobs and $38^{\circ}\text{Be HNO}_3$ was larger (1-liter) than the flask used for the As_4O_6 - acid mixture. Fresh cobs and acid were added at intervals and the batch was heated in order to generate large volumes of fumes.

After pretreatment the cobs were treated with 1.50 HNO_3 in a set-up similar to that shown in Figure #5. 20 grams of cobs were treated in each run. This series comprised Experiments #7, 8, 9, 10 and 11.

Number	Remarks	Results
#7	Treated cobs with fumes 5 hours. Let stand over night in the fumes.	Cobs soft and moist after treatment.
	Added 100 grams 1.5 HNO_3 and V_2O_5 . Good yield of crystals in 48 hours.	Cobs slowly decomposed. Catalytic reaction very moderate. Yield = 65.8%.
#8	Treated with fumes 5 hrs. Did not let stand over night in the fumes.	Cobs soft and moist.
	Added 80 grams 1.5 HNO_3 and V_2O_5 (0.2 gm). Some crystals and some syrupy residue in 48 hrs.	Catalytic reaction so violent flask had to be cooled. Yield = 64.75%.
#9	Treated with fumes 3 hrs. Let stand overnight in fumes.	Cobs soft and moist.
	Added 80 grams 1.5 HNO_3 and V_2O_5 (0.2 gm.) Good yield of crystals in 48 hours.	Catalytic reaction so violent flask had to be cooled. Yield = 76.3%.

Number	Remarks	Results
#10	Treated with fumes 3 hrs. Let stand overnight in fumes.	Cobs soft and moist.
	Added 100 grams 1.5 HNO_3 and 0.2 gm. V_2O_5 . Cooled flask after catalytic reaction had proceeded awhile.	Catalytic reaction after long interval. Not as violent as usual. Good yield of crystals in 48 hours. Yield = 74.1%.
#11	Treated with fumes 6 hours.	
	Added 100 gms. 1.5 HNO_3 and 0.2 gm. V_2O_5 . Heated strongly with gas flame until catalytic reaction set in. Then cooled flask with water.	Fair yield of crystals in 48 hours. Yield = 50%.

The deductions from the foregoing series of experiments are:

Long continued pretreatment with fumes seems to moderate the catalytic reaction when the ratio 5 to 1 is used. This is probably due to the moisture in the gases being soaked up by the cobs with consequent dilution of the 1.5 HNO_3 .

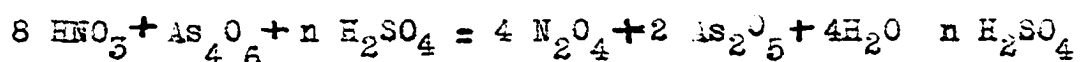
The ratio 4 to 1 seems to give as high yields as the ratio 5 to 1, although neither gave a 100 per cent yield of oxalic acid.

The purpose of the next investigation was to ascertain if nitrous oxides, when passed into a mixture of cobs, catalyst, and nitric acid of either 57 per cent or 70 per cent strength, would decompose the cobs sufficiently to give a high yield of oxalic acid. In case this could be done, the

need of concentrating the absorption tower acid would be done away with. This would decrease the cost of producing the oxalic acid almost \$100 a ton.

The procedures and results of the investigation are as follows:

The set-up employed is shown in Figure #6. The cobs, catalyst, and acid were placed in flask B. Flask A contained a mixture of As_2O_3 , 1.5 HNO_3 , and 1.84 H_2SO_4 , to generate N_2O_4 according to the reaction.



The fumes were passed up through the mixture in flask B for varying intervals. The treatment of the fumes and the contents of flask B is indicated in the tabulated procedures together with the results. 10 grams of cobs, and 0.1 gram of V_2O_5 were used in each run.

Experiments 1, 2, 3, 4, 5, 6, 7, and 8.

Number	Grams Acid	Remarks	Results.
#1	50 of 57%	Treated with cold N_2O_4 for 2 hours. Dark green liquid and cob pulp as residue.	Cobs pulped to some extent. No oxalic acid.
#2	50 of 57%	Treated with hot N_2O_4 for 2 hours, heating flask B to boiling at intervals.	Cobs broke down to fine pulp. No oxalic acid.
#3	50 of 57%	Same as for #2	No oxalic acid.
#4	50 of 70%	Same as for #2 and #3	No oxalic acid.

Number	Grams Acid	Remarks	Results
#5	50 of 1.5 HNO_3	Same as for #4	Cobs were more pulped, but some were undecomposed. Small yield of crystals.
#6	50 of 57%	Passed air and N_2O_4 through for 3 hours heating flask B at intervals.	Cobs pulped but all did not go into solution. Very few crystals after 48 hours.
#7	50 of 57%	Passed cooled N_2O_4 through for 3 hours heating flask B to boiling at intervals.	Residue of cob pulp and dark green liquor. No oxalic acid.
#8	30 of 1.5 HNO_3	Passed air and N_2O_4 through for 3 hours, heating flask B at intervals.	Results were same as in #6. Very few crystals after 48 hours.

In the next three runs H_2SO_4 was added to the HNO_3 in flask B. The procedure was the same as before.

#9	50 of 1.5 HNO_3 8 of 1.84 H_2SO_4	Passed N_2O_4 thru for 2 hours, heating flask B at intervals.	Residue of cob particles and dark greenish brown liquor. Small yield of crystals after 48 hours.
#10	50 of 57% HNO_3 30 of 1.84 H_2SO_4	Same as for #9	No crystals after 48 hours.
#11	50 of 57% HNO_3 10 of 1.84 H_2SO_4	Same as for #9	Cob pulp and dark green liquor remained. No crystals after 48 hours.

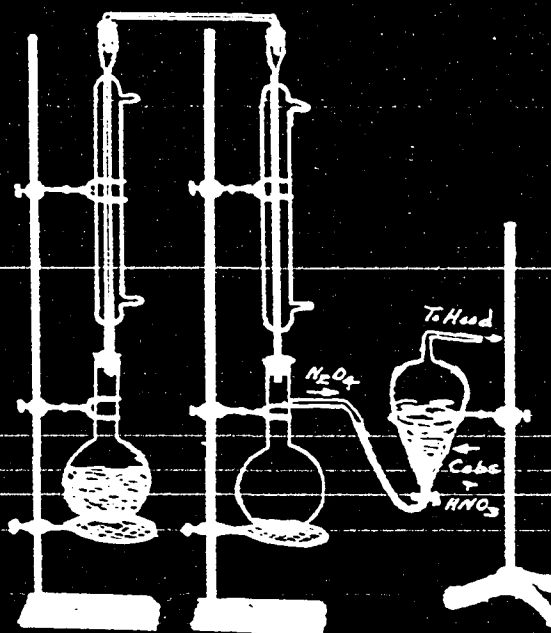


Figure 6.

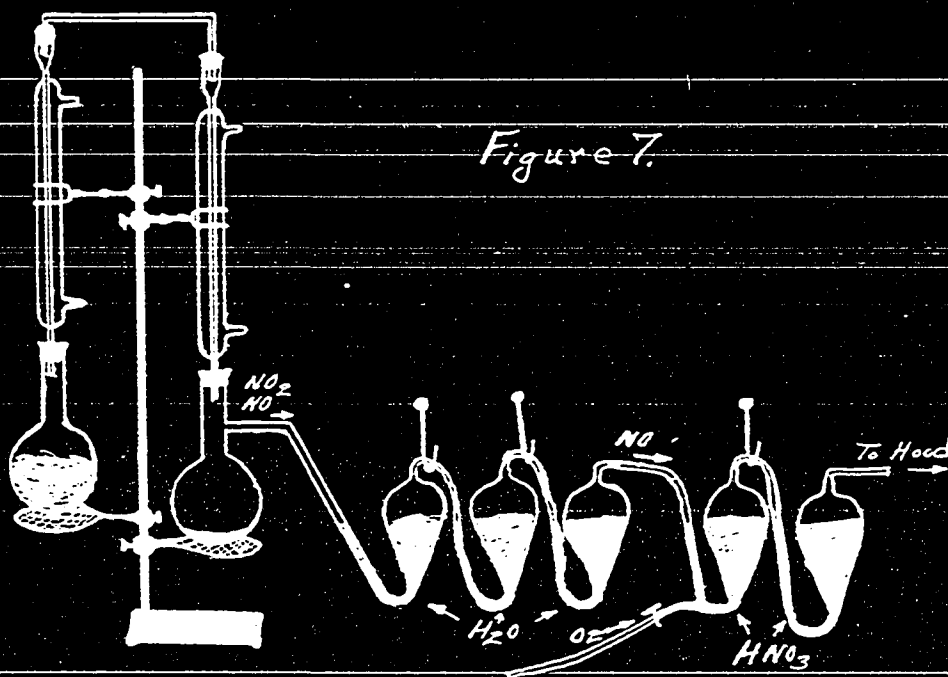


Figure 7.

In another experiment, using the same set-up, 20 grams of cobs, 0.2 gram V_2O_5 , and 100 grams of 57 per cent HNO_3 , were placed in flask B. Then N_2O_4 fumes were passed through for one hour. The N_2O_4 fumes were then shut off. 60 grams of 1.5 HNO_3 were added and the flask B heated at intervals, then 20 grams more of acid were added. After several periods of heating, a final 20 grams were added and the flask was heating to boiling for several minutes. Then N_2O_4 fumes were passed through for another hour.

The first treatment broke the cobs down to large pulpy white particles. The 1.5 HNO_3 caused finer pulping but did not bring the cobs into solution. A greenish yellow liquid and fine cob particles remained after the run.

Several experiments were then made in which both 57 per cent HNO_3 (38°Be), and 70 per cent HNO_3 (1.42 sp. gr.) were saturated with NO_2 .

20 gram portions of ground cobs, mixed with 0.2 gram V_2O_5 were then treated with these NO_2 saturated acids, the ratio of acid to cobs varying from 4 to 1 up to 8 to 1. In some of the runs, the reaction was allowed to proceed at will; in others the mixture was heated up to the boiling point of the acid. The reactions were all vigorous and the cobs were pulped to fine particles. The dark brown acids changed in each case to green liquors. No oxalic acid crystals separated from any of these mixtures in 48 hours, so none were analyzed.

If any acid formed, it was in very small amounts.

The conclusions derived from this series of experiments are:

HNO_3 of 57 per cent and 70 per cent strength cannot be fortified sufficiently with NO_2 (N_2O_4) to break down all the ground cobs to oxalic acid.

Treating a mixture of cobs and HNO_3 (of the above strengths) with NO_2 does not produce sufficient fortification to cause breakdown of the cobs to oxalic acid.

It is evident that the N_2O_5 and not NO_2 (N_2O_4) is responsible for the oxidation of the cobs to oxalic acid, although the presence of lower oxides than N_2O_5 probably has a catalytic effect in favor of the oxidation.

Correspondence was opened with the General Chemical Company, to ascertain their method of making the 1.5 HNO_3 used in the experiments. Their reply is given verbatim:

"Your letter of July 29 is at hand in which you state that you have attempted to fortify 70 per cent nitric by passing nitrogen peroxide through the acid. This is of course impossible.

Our process consists of producing nitric oxide and mixing it under definite conditions with 1/4 of its volume of oxygen, thereby producing nitrous acid anhydrous (N_2O_3) which under our conditions is acted upon by water vapor or water in the C. P. nitric producing nitric acid, nitrous acid

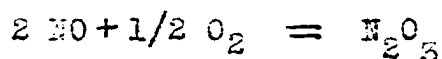
and a further amount of nitric oxide. Under the conditions the nitrous acid again decomposes somewhat to nitric acid, nitric oxide and water.

While the above reactions may not be absolutely true and many side reactions can take place, it is evident from the resultant products that the above reactions are substantially produced.

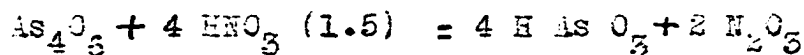
We produce our nitric oxide originally by the action of nitric acid upon metallic copper introducing the oxygen directly into the reaction chamber containing the copper and nitric acid from whence we lead the resultant gases into C. P. 70 per cent nitric acid which after a short time becomes of the approximate composition of 90 per cent nitric acid and 10 per cent of lower oxide. In this way we can fortify about one gallon of acid to the above strength in approximately eight hours."

In order to test this method the following experiment was performed.

Instead of generating NO and adding 1/4 its volume of oxygen to produce N_2O_5 according to the reaction



the more convenient (although more expensive) method of Cundall was adopted.



The N_2O_5 fumes produced were cooled and then bubbled

through 1.42 HNO_3 (70 per cent) for two hours. The colorless 70 per cent nitric gradually changed to a dark greenish yellow color. The HNO_3 was analyzed before and after the 2 hour run with these results:

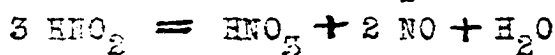
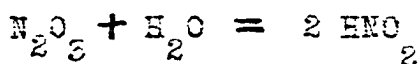
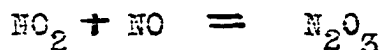
$$\text{HNO}_3 \text{ (before)} = .908 \text{ Kg. HNO}_3 \text{ per liter} = 64.75 \text{ per cent } \text{HNO}_3$$

$$\text{HNO}_3 \text{ (after)} = .952 \text{ Kg. HNO}_3 \text{ per liter} = 67.50 \text{ per cent } \text{HNO}_3$$

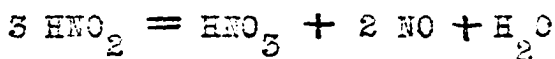
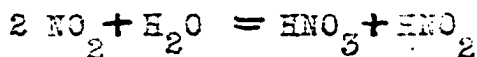
The HNO_3 was thus fortified 2.75 per cent in two hours.

At this rate it would have taken 17 hours to fortify the acid to 90 per cent, although the rate may increase as the acid gets stronger. Due to scarcity of As_2O_3 the run was only continued for the two hours.

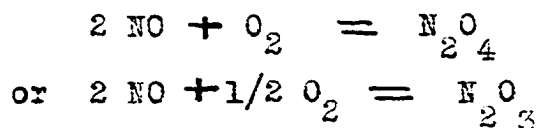
Two experiments were then made using the set-up shown in Figure #7. The fumes generated by heating a batch of cobs with 38°Be HNO_3 were first passed through three absorption flasks containing water to remove most of the NO_2 according to the reactions.



also



The NO evolved from the above reactions was then mixed with oxygen and bubbled into 38°Be HNO_3 . By adjusting the flow of oxygen either of two reactions are possible.



The second reaction was desired so an effort was made to adjust the oxygen to about 1/4 the volume of gases passing from the water absorption bottles. This was difficult due to the irregularity of flow of gases from the mixture of cobs and acid. There was probably CO_2 present in the evolved gas in unknown amount.

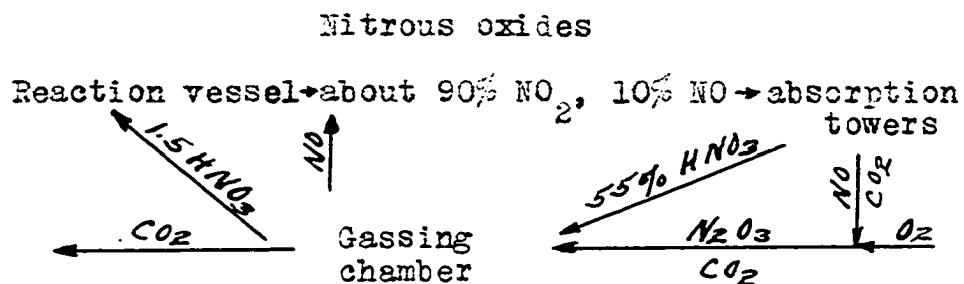
In the first experiment, the $38^\circ \text{ Be HNO}_3$ was gassed for two hours; in the second, the $38^\circ \text{ Be HNO}_3$ was gassed for six hours.

Results:	#1	#2
Initial acidity of $38^\circ \text{ Be HNO}_3$	54.93%	54.93%
Acidity after gassing	47.49%	42.75%
Initial acidity	Nil.	Nil.
Final acidity of liquor in		
the first wash bottle	42.10%	46.72%

The results show that the acidity of the water used as absorbent was gradually increasing from zero to the maximum of 68.4% strength, while the acidity of the $38^\circ \text{ Be HNO}_3$, instead of increasing, was gradually decreasing. This may have been due to evaporative effects of too fast a rate of gassing, or it may have been caused by equilibrium effects brought about by gassing with gases of the wrong composition. However, it is not known for certain yet as to what did cause

these decreases in acidity. The General Chemical Company may gas under pressure, or at a very slow rate, and in any case the nature of the gases used by them, permits them to employ the exact proportions required.

No further work was done along this line. It is evident that this method can be used if the composition of the evolved gases is adjusted to give N_2O_3 . It is not known what effect any CO_2 would have on the process. At any rate an absorption system would have to be used to recover the NO evolved. The wholesale price of 1.5 HNO_3 made in this manner is about 60 cents a pound in five pound lots. The cost of the gallon glass-stoppered bottle plus a special earth for packing and a tin container are included in this cost. No estimate of the cost of producing 1.5 HNO_3 from the fumes evolved when cobs are treated with 1.5 HNO_3 , by this method is available yet. A suggested flow sheet is as follows:



The next experiments were efforts made to increase the yield of oxalic acid per pound of corn cobs. The best yields that have been obtained so far by treatment with nitric

acid alone are one pound of oxalic acid from one pound of cobs, or, as usually stated, 100 per cent yield. When HNO_3 functions as an oxidizing agent, water is one of the products of the reaction. As the amount of water increases during the reaction, the remaining HNO_3 becomes more and more dilute and hence becomes less efficient as an oxidizer. This suggests using a dehydrating agent to remove the water as fast as it is formed.

The dehydrating agents most suitable for the process under consideration are H_2SO_4 and P_2O_5 , so several runs were made using nitric acid mixed with either of these two compounds. The apparatus used is shown in Figure #5.

Procedure:

10 grams of ground cobs, and 0.1 gram V_2O_5 were placed in the reaction flask. Then the mixed acids, as shown in tabulated form, were added. The treatment given the mixtures, together with observations and results were as follows:

Number	Acids	Remarks	Results
#1	40 gms. 1.5 HNO_3 8 gms. 1.84 H_2SO_4 .	Let react until cobs were in solution, then cooled.	Fair yield of crystals. Not analyzed.
#2	Same as #1	Same as #1.	Fair yield of crystals. Not analyzed.
#3	Same as #1	Let react without cooling. Cobs charred to some extent.	Dark brown mass of viscous material. No crystals.

Number	Acids	Remarks	Results
#4	30 gms. 1.5 HNO ₃ 8 gms. 1.84 H ₂ SO ₄	Flask cooled when reaction became very vigorous.	Not analyzed as no crystals formed. Some pulp remained.
#5	50 gms. 38 ⁰ Be HNO ₃ 30 gms. 1.84 H ₂ SO ₄	Heated strongly. Cobs charred to some extent.	Brown viscous mass. No crystals.
#6	Same as #5	Heated to boiling, then cooled.	Cobs pulped but did not go into solution.
#7	Same as #6	Let react without external heating. Cooled when reaction became violent.	Cobs were pulped but no crystals formed.
#8	40 gms. 1.54 HNO ₃ 8 gms. P ₂ O ₅	Let react until violent, then cooled.	Small yield of crystals.
#9	50 gms. 1.5 HNO ₃ 5 gms. 1.84 H ₂ SO ₄	Same as #8.	Good yield of crystals. Yield = 68.7%.
#10	50 gms. 1.5 HNO ₃ NO 1.84 H ₂ SO ₄	Same as #8.	Good yield of crystals. Yield = 61.6%.
#11	70 gms. 1.5 HNO ₃	Same as #8.	Good yield of crystals. Yield = 55%.
#12	40 gms. 1.5 HNO ₃ 8 gms. 1.84 H ₂ SO ₄	Same as #8.	Good yield of crystals. Yield = 70.5%
#13	40 gms. 1.5 HNO ₃ 4 gms. 1.84 H ₂ SO ₄	Same as #8.	Good yield of crystals. Yield = 57.2%.

Number	Acids	Remarks	Results
#14	50 gms. 1.5 HNO ₃ 5 gms. 1.84 H ₂ SO ₄	Same as #8	Good yield of crystals. Yield = 61.1%
#15	50 gms. 1.5 HNO ₃ 10 gms. 1.84 H ₂ SO ₄	Same as #8	Fair yield of crystals. Yield = 44.8%
#16	50 gms. 1.5 HNO ₃ 20 gms. 1.84 H ₂ SO ₄	Cooled at first stage of violent reaction.	No crystals in 24 hours. Foamy liquid residue.

Added 10 gms. 1.5 HNO₃ after 24 hours. No crystals were present after 48 hours more, only a pulpy greenish yellow residue remained.

The next experiment was suggested by United States Patent, 1,356,137, October 18, 1921, G. H. Gontard and A. Keller.

"Oxalic acid is prepared by treating 100 parts by weight of sucrose with 320 parts of 100 per cent H₂SO₄, 300 parts of HNO₃ of 100 per cent strength, and 380 parts of H₂O in the presence of a catalyst such as V₂O₅ or salts of Mo or Mn."

Instead of using the above proportions, 10 grams of ground cobs, with 0.1 gram V₂O₅, were treated with 50 grams 1.84 H₂SO₄ (95 per cent), 30 grams 1.5 HNO₃ (95 per cent) and the amount of water was cut from 38 grams to 30 grams. The reaction was allowed to proceed at will. The reaction was vigorous, but after 30 minutes the brown fumes cleared away leaving a pulpy mass of cobs only slightly decomposed. The

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results were not at all promising so no further efforts were attempted with this mixture.

The conclusions derived from this series of experiments are:

H_2SO_4 in large proportions causes charring of the cobs.

H_2SO_4 in small amounts does not affect the reaction to any great extent.

The presence of H_2SO_4 (in any proportion) neither increases the yield of oxalic acid nor decreases the amount of 1.5 HNO_3 necessary for a good yield.

The presence of H_2SO_4 increases the difficulty of controlling the reaction.

The presence of H_2SO_4 does not decrease the strength of nitric acid needed to obtain a high yield.

P_2O_5 is less effective than H_2SO_4 .

B. Treatment of Corn Cobs With 30 to 70
Per Cent Nitric Acid

1. The Effect of the Nitric Acid Concentration: This phase of the work was concerned with the treatment of cobs with nitric acid of less strength than 1.5 specific gravity which is usually between 95-100 per cent in strength. As stated in a previous section the cost of concentrating nitric acid up to 90 per cent or greater strength is approximately two-thirds of the entire cost of recovering nitrous gases. If satisfactory yields of oxalic acid could be secured with nitric acid of the strengths usually recovered from absorption towers (50-60 per cent) the cost of producing oxalic acid by this process would be materially decreased.

The first experiments were made using 30 per cent nitric acid and then succeeding runs were made using 40, 50, 60 and 70 per cent acids. 30 per cent nitric acid represents about the worst possible recovery under which an absorption system would have to operate and in the arc process for the fixation of atmospheric nitrogen nitrous gases as low as one per cent in 50 are recovered as 30-35 per cent acid. On the other hand 70 per cent acid represents the theoretical maximum strength obtainable from absorption towers and it has been found to be uneconomical to try to get an acid stronger than 55-60 per cent due to the technical difficulties encountered.

In all the following runs 40 grams of cobs ground to about 20 mesh and 240 grams of nitric acid were used. This

amount of acid was found to wet the cobs satisfactorily and thus ignition or charring of the cobs was prevented. The experiments were carried out in one liter balloon flasks fitted with reflux condensers and heated by means of gas burners.

There are several possible variables in carrying out a reaction of this sort such as: ratio of acid to cob, concentration of acid used, temperature maintained during the reaction, pressure on the system, reaction time, catalysts used, degree of fineness of the cobs, agitation, whether the nitric acid is refluxed or distilled off and fresh acid added during the run, successive treatment of the cobs with acids of various strengths and perhaps several others may be suggested.

In this series of experiments, however, in order to study the effect of acids of different concentrations all the other conditions were kept as constant as possible and only the strength of the nitric acid was varied. No catalyst was used in these experiments and agitation was used only with the 50 per cent acid when an electric stirrer was employed to see if vigorous stirring would increase the yield of oxalic acid.

In all the experiments copious red fumes of N_2O_4 were given off, the volume seeming to increase with the strength of acid used. The fumes first became pronounced for the 30 per cent acid when the temperature reached 75°C but for the stronger acids the temperature was somewhat lower. After the external heating was discontinued and visible action in the flasks had ceased there remained in most cases a residue of undecomposed

cob the amount of which decreased in general with increase in strength of acid used. In the cases where a very severe treatment was used, such as long heating and strong acid a small amount of carbonaceous material would form due to slight charring on the sides of the flask.

After the heating period, the products were allowed to stand without dilution or other treatment for seventy-two hours. The batches were then filtered on a wool cloth using a Buchner funnel. The residues were washed first with 400 cc. of cold water and then with 200 cc. of boiling water. The filtrate and washings were mixed together, made up to one liter and aliquot samples were analyzed for oxalic acid. The washed residues were removed from the filter cloth and dried at 105°C . The weights of the residues, after being dried, were calculated back to per cents of the air dried cobs (4.97 per cent moisture).

The data and results of this series of experiments are listed in the following table:

No.	: Acid Strength % HNO_3	: Heating Period in Hours	: Max. Temp. $^{\circ}\text{C}$	Remarks	Results	
					: Yield Oxalic Acid :($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$):	: Yield Residue :(Air Dry)
1	: 30	: 1/2	: 101	: Light yellow pulp	: 15.5	: 36.7
2	: 30	: 1	: 102	: Light yellow pulp. NO_2 fumes: at 40°C .	: 18.6	: 34.8
3	: 30	: 2	: 101	: Light yellow pulp	: 16.4	: 33.8
4	: 30	: 4	: 103	: Residue some- what lighter	: 16.5	: 27.0

No.	: Acid : % HNO_3 :	: Heating : Period : in Hours:	: Max. : Temp. : $^{\circ}\text{C}$.	Remarks	Results	
					: % Yield : Oxalic acid : $(\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O})$:	: % Yield : Residue : (Air Dry)
5	40	1/2		: Yellow residue: : Slight disin- : tegration	18.6	36.8
6	40	1		: Whiter residue: : More disinter- : gration	20.5	37.5
7	40	1 1/2		: Whiter residue:	20.9	36.0
8	40	2		: White residue: : Cobs entirely : pulped	19.4	32.8
9	40	2 1/2		: Smaller residue	26.6	26.8
10	40	3		: Same as #9	26.7	25.0
11	50	1/4		: Cobs not en- : tirely pulped	23.8	35.5
12	50	1/2		: Cobs slightly : pulped	24.9	34.0
13	50	1		: Cobs entirely : pulped	28.4	32.0
14	50	2		: Slightly yellow : residue	29.0	26.0
15	50	2 1/2		: Small amount : of residue	33.2	20.7
16	50	3		: Same as #15	33.4	19.5
17	60	1/2		: White residue	34.2	32.2
18	60	1		: Light grey : residue	37.3	26.8
19	60	1 1/2		: Slightly : yellow residue	35.2	26.0
20	60	3		: Small residue	37.8	18.2
21	70	1/4		: Small amount : light yellow : pulp	45.3	23.7
22	70	1/2		: Same as #21	46.7	21.0
23	70	1		: Same as #21	43.0	20.2
24	70	1 1/4		: Same as #21	41.0	18.5
25	70	2		: Same as #21	45.8	12.2
26	70	2 1/2		: Same as #21	39.4	12.5
27	70	3		: Same as #21	45.0	13.2

A study of the foregoing results brings out the following facts: The yield of oxalic acid increases as the strength

of the nitric acid is increased from 30 to 70 per cent while maintaining the same weight ratios of acid to cobs; the yield of pulp residue decreases as the strength of the acid used is increased from 30 to 70 per cent; the yield of oxalic acid varies but slightly with the increase in the heating period from 1/2 to 2 1/2 or 3 hours; the yield of pulp residue decreases consistently as the heating period is prolonged from 1/2 to 2 1/2 to 3 hours except in the case of the 70 per cent nitric acid. In this case the pulp residue appears to decrease to a minimum of a 12-13 per cent yield in two hours and another hour of heating did not affect the pulp yield.

The weaker concentrations of nitric acid (30 and 40 per cent) rapidly reduce the cobs to a residue that averages about 35 per cent of the original weight of the cobs. Corn cobs are composed of about 35 per cent cellulose, 35 per cent of lignin bodies and 27 per cent of hemicelluloses of which the greater part is xylan. It is known that lignins are easily attacked by nitric acid with the formation of oxalic and other acids. Also xylan is readily hydrolyzed by weak nitric acid to xylose and continued treatment with nitric acid of higher concentration decomposes the xylose with formation of oxalic and other acids such as the aldonic acids. It would appear from the pulp yields secured with the 30 and 40 per cent nitric acids that the residue is composed mostly of cellulose as cellulose is more resistant to nitric acid than the lignins and hemicelluloses.

The average yields of pulp resulting from the treatment of cobs with the 30 and 40 per cent nitric acids correspond very closely to the cellulose content of the cobs. This conclusion is strengthened also by the slow decrease in pulp yield as the heating period is prolonged. In these cases the cellulose itself is being slowly degraded by the acid.

When the stronger acids (60 and 70 per cent) are used the degradation of the cellulose is much more pronounced as in these cases the hydrolyzing action of the nitric acid is probably of secondary importance to its oxidizing action and the cellulose together with the lignins and hemicelluloses are being oxidized to oxalic and other organic acids. This would account for the relatively rapid increase in oxalic acid yield (over 100 per cent, or from 20 per cent to 45 per cent based on the weight of the cobs) as the strength of the acid used is increased from 40 to 70 per cent.

The fairly constant weight of residue which remains after treatment of the cobs with 70 per cent nitric acid is probably composed almost entirely of oxycellulose which is known to be more resistant to oxidation than the original cellulose. It is probable also that the cellulose residues resulting from the treatment with the weaker nitric acids contain some oxycellulose as the cellulose could not hope to escape some oxidation while being freed of the lignins and hemicelluloses.

To verify this conclusion qualitative tests for oxycellulose were made on some of the residues and positive results

were secured in each case. The test is made as follows.

The cellulose to be examined is washed free of nitric acid and is then suspended in distilled water. On the addition of a drop of methyl orange the liquid turns yellow or reddish yellow. A few cubic centimeters of a concentrated solution of sodium chloride are then introduced and the color, in the presence of oxycellulose, changes to wine red. The test depends on the fact that in the presence of sodium chloride, the carboxyl group in oxycellulose turns methyl orange wine red. The method may be rendered quantitative by titration with standard alkali but the distinction is not very sharp. Other forms of cellulose do not produce this change.

Two quantitative tests for oxycellulose were run on two different residues. These residues were as follows:

(1) Run #8, 40 per cent HNO_3 , 2 hr. heating period, 52.8 per cent yield of residue.

(2) Run #12, 50 per cent HNO_3 , 1/2 hr. heating period, 34 per cent yield of residue.

The quantitative tests were made by determining the copper number of the pulp residues. The copper number is generally agreed upon as a measure of the oxycellulose content of a cellulose material. This is some controversy over whether it indicates absolute values or not but it is generally used as an index of oxycellulose formation.

The procedure used is that recommended by Schorger (17)

and is as follows.

The sample weighing 3 grams, less if possessing high reducing properties, is placed in a 1.5 liter balloon flask equipped with a short reflux condenser and stirrer. Into the top of the condenser is inserted a small, short-stemmed funnel through which passes the shaft of the stirrer. The flask is then placed in a bath at 100°C .

In another 1.5 liter balloon flask, are placed 350 cubic centimeters of water, 20 cubic centimeters of copper sulphate solution, and 30 cubic centimeters of alkaline tartrate solution. The contents of the flask are heated to 100°C and added to the sample in the other flask. The flask is then heated in a water bath for 45 minutes with stirring sufficiently rapid to keep the contents in gentle motion. The flask is then removed and the solution immediately filtered on a Buchner funnel through two sheets of Whatman #5 filter paper. The material on the filter is washed first with one liter of cold water and then 750 cubic centimeters of boiling water.

The Buchner funnel is then transferred to a 250 cubic centimeter filter flask. The contents are treated with 25 cubic centimeters of ferric alum solution, in the case of standard cellulose; materials having a higher copper number, or fine texture, may require more ferric alum to remove the cuprous oxide. In such cases, it is added in 25 cubic centimeter portions and a blank determined to correct for the additional ferric alum. The ferric alum retained by the material is washed out

with 100 cubic centimeters of 2N sulphuric acid, applied in two 50 cubic centimeter portions. The Buchner funnel is then removed and the contents of the flask titrated to a light pink with 0.04N potassium permanganate.

$$\frac{\text{c.c. } \text{KMnO}_4 \text{ used} \times 0.00254 \times F \times 100}{\text{Weight of sample}} = \text{Copper number}$$

1 cc 0.04N KMnO_4 = 0.00254 gram copper.

F = factor of KMnO_4

Standard cellulose prepared from cotton has a copper number of 0.0045. The copper numbers of some typical cellulose materials are given in the following table.

Material	Corrected Copper Number
1. Oxycellulose (By bleaching powder)	10.99
2. Nitrating cotton	0.28
3. Wood pulp oxycellulose (By bleaching powder)	55.22
4. Wood pulp (for nitration)	1.00
5. Oxycellulose (by KMnO_4)	8.05
6. Oxycellulose (by H_2O_2)	5.30
7. Hydrocellulose (Girard).....	5.64
8. Wood pulp (Ritter-Zellner, unbleached) ...	1.14
9. Wood pulp, normal bleach	2.14
10. Wood pulp, overbleached	3.85

The results of the copper number determinations made on the two pulp residues were as follows:

- (1) Run #8, (40 per cent H_2O_2) Copper number = 10.06
 (2) Run #12, (50 per cent H_2O_2) Copper number = 9.91

These results indicate that the pulps contained very nearly the same per cent of oxycellulose. The following table compares the total results obtained in these two runs.

No.:	Strength:	Heating	Yield of	Copper	Yield of
:	Acid %	Periods,	Residue %	Number	Oxalic Acid %
:	:	Hours	:	:	:
8 :	40 :	2 :	32.6 :	10.06 :	19.4
12 :	50 :	1/2 :	34.0 :	9.91 :	24.9

The table shows a rather close correlation between the yield of residue and the copper number but the yield of oxalic acid appears to be independent of the factors influencing the copper number to some extent. The stronger acid (50 per cent) exerts a more rapid action on the cobs than the weaker acid (40 per cent) which is to be expected.

From the qualitative tests for oxycellulose made on several of the residues and from the two quantitative tests previously recorded, and considering the rapid and marked effect of nitric acid on lignins and hemicelluloses it is evident that the residues from the various runs were composed mainly of cellulose and its degradation products, oxycellulose and probably hydro-cellulose. The amounts of the degradation products undoubtedly increase at the expense of the cellulose as the heating period and the strength of the nitric acid used are increased. As the strength of acid is increased there is also more or less complete break-down of the cellulose and its products to oxalic acid and other organic acids with oxalic acid predominating.

The results of this series of experiments on the production of oxalic acid from cobs by oxidation with nitric acid of strengths ordinarily obtained from absorption systems indi-

cate that commercially the use of these weaker acids would be as economical as the use of fuming nitric acid although the yields of oxalic acid are much less.

The 60 per cent nitric acid would probably be the most favorable strength to use. Although the 70 per cent acid gives greater yields of oxalic acid it is practically impossible to recover this strength acid direct from the towers without some further concentration. Even the recovery of the nitrous gases as 60 per cent nitric acid requires an exceedingly well designed and operated absorption system. The 50 per cent nitric acid gives somewhat smaller yields of oxalic acid than does the 60 per cent but this strength acid can be readily obtained from absorption towers. The 30 and 40 per cent nitric acids should probably not be given much consideration. They give rather low yields of oxalic acid and represent the output of recovery systems dealing with nitrous gases of very low concentrations. Even if they were used as starting acids the fumes from their reaction on coals are rich enough in nitric oxide to be recovered readily as 50 to 55 per cent nitric acid.

Perhaps, all things being considered, 55 per cent nitric acid should be the strength to use in this process. This strength of acid represents the output of an average absorption system working under favorable conditions such as should prevail in this process. Also the yield of oxalic acid should be close to that obtained with 60 per cent nitric acid or an average yield of 35 per cent for a one hour heating period.

A comparison of the costs of producing oxalic acid using fuming nitric acid (95-100 per cent) and 55 per cent nitric acid, based mainly on the cost of recovery and the yields of oxalic acid, is given in the following tabulated form. The estimate on fuming nitric acid is that given previously.

For fuming nitric acid (95-100 per cent):

Ratio of acid to cobs is 5:1.

Yield of oxalic acid is 100 per cent based on the weight of the cobs.

	Amount	Cost
HNO_3 used per ton of oxalic acid produced	5 tons	\$ 550
HNO_3 recovered as 1.5 sp. gr. HNO_3	<u>4.7 "</u>	<u>517</u>
HNO_3 necessary for make-up acid.	0.3 "	35
Cost of recovering the 4.7 tons HNO_3 as 95-100% HNO_3		<u>150</u>
Total HNO_3 cost per ton of oxalic acid produced		183

Taking the average market price of oxalic acid at 11 cents per pound F.O.B. works.

Sales price per ton of oxalic acid	\$220
Less cost per ton of oxalic acid (183 10) (Assuming cobs at \$10 per ton)	<u>193</u>
Gross profit per ton of oxalic acid produced.	27

For 55 per cent nitric acid:

Ratio of acid to cobs is 6:1.

Yield of oxalic acid is 35 per cent based on the

weight of the cobs.

	Amount	Cost
HNO_3 used per ton of oxalic acid produced (The cost is estimated at 55 per cent of \$110)..	17.143 tons	\$1037
HNO_3 recovered as 55 per cent acid (Assuming 94 per cent recovery as in the first case).....	16.114 "	975
HNO_3 necessary for make-up acid ...	1.029 "	62
Cost of recovering the 16 tons HNO_3 as 55% HNO_3 (Includes cost of absorption only)		88
Total HNO_3 cost per ton of oxalic acid produced..		\$150

The estimated nitric acid recovery cost per ton of oxalic acid produced when using 55 per cent acid is, therefore, about \$53 less than when the 95-100 per cent acid is used. As stated before this estimated cost is based mainly on the cost of recovering the nitric acid so that it can be used over again in the cyclic process. It is assumed in both cases that the cost of working the reaction vessels would be about the same. No figures are available for estimating the cost of working the reaction vessels, but the figure of \$5.50 per ton for recovering 55 per cent nitric acid from the ammonia oxidation process includes both the cost of working the converter and the absorption system proper. The cost of working the reaction vessels in the production of oxalic acid would probably be about the same as the cost of working the converters in the ammonia oxidation process and the cost of working the absorption systems to re-

cover the acid as 55 per cent nitric acid should be about the same in both cases.

The residue left after the treatment of cobs with 55 per cent nitric acid can be added to a fresh batch of cobs about to undergo oxidation as it is already partially oxidized.

2. Effect of Catalyst Added to Reaction Mixture: 200

grams of cobs were digested with 800 grams of 40 per cent nitric acid at the boiling point. Vanadium pentoxide was used as the catalyst. The heating caused a violent reaction and it was necessary to cool the flask by running cold water over it. After the violence of the reaction had decreased the mixture was slowly boiled for one hour. The mixture was next heated at 60°C for four hours, then it was filtered and the filtrate was allowed to stand 24 hours before being analyzed. The oxalic acid content was 23.2 grams or 11.6 per cent of the weight of the air dry cobs.

The vanadium pentoxide used in all cases as a catalyst was made by decomposing ammonium vanadate at a low temperature. The resulting vanadium pentoxide was kept in a glass stoppered bottle. When made in this manner it was much more effective as a catalyst than stock vanadium pentoxide.

The yield in this experiment was somewhat lower than when no catalyst was used, other conditions being the same. The lower yield was probably due to the prolonged heating after the violent reaction had subsided as will be shown later.

A series of experiments were made using 60 per cent nitric acid both with and without a catalyst. Sixty per cent acid was used because that concentration represents about the strength of nitric acid that can be recovered from a well designed recovery system when operating on nitrous gases rich in

nitric oxide (NO).

In all of these experiments 20 grams of air dry corn cobs (moisture content 7 per cent) ground to pass a 20 mesh sieve were used. The ground cobs were mixed with the proper amount of 60 per cent nitric acid (plus the catalyst if used) in a 1-liter round bottom flask with a reflux condenser attached. When heating was employed, the mixture was heated to the boiling point of the acid with a low gas flame, and if the heating period was long continued the gas flame was kept so low that the liquor in the reaction flask gently simmered.

In each case the reaction mixture was allowed to remain in the reaction flask without the addition of any water for three days. Then 300 c.c. of water were added to each flask and the mixtures were allowed to stand 24 hours longer. The mixtures were then filtered on a Gooch crucible through muslin cloth. The first portions of the filtrates were refiltered through the residues until the filtrate ran clear. The residues were washed until the total volume of filtrate plus washings was one liter. These liquors were then set aside, and the residues were washed with several liters of water, then with two liters of one per cent ammonia water, and then with several more liters of water until the wash waters ran through neutral.

The procedures and results of this series of experiments are given in the following table:

No.	Grams :Cobs	Grams :HNO ₃	Heating :period at: :boiling :point in :minutes	Remarks	Results	
					% Yield :Oxalic :Acid :(C ₂ H ₂ O ₄ · :2H ₂ O)	% Yield :Residue :(air dry)
1	20	120	None	No heat or cata- lyst used.	23.50	24.7
2	20	120	None	No heat used V ₂ O ₅ as catalyst	37.68	28.8
3	20	120	5	No catalyst	16.22	30.0
4	20	120	5	V ₂ O ₅ used	28.25	31.1
5	20	120	60	No catalyst	16.87	27.4
6	20	120	60	V ₂ O ₅ used	8.11	26.9
7	20	240	None	No heat or catalyst	29.80	33.5
8	20	240	None	V ₂ O ₅ used	54.00	31.0
9	20	240	5	No catalyst	35.80	25.8
10	20	240	5	V ₂ O ₅ used	31.10	26.1
11	20	240	30	No catalyst	64.60	14.5
12	20	240	30	V ₂ O ₅ used	6.43	18.3
13	20	240	5	V ₂ O ₅ used	55.2	25.3

Run #13 was a duplicate of run #10 except that after the 5 minute boiling period the flask was immersed in cold water and kept there for 3 days. In run #10, after the 5 minute boiling period, the gas flame was removed, and the vigorous reaction in the flask was allowed to proceed until the flask and contents had cooled by natural radiation, which required about an hour.

The residues of the first six runs were analyzed for lignin, pentosan, and alpha-cellulose contents. The results were as follows:

No.:	Lignin		Pentosans		Alpha-cellulose	
	% in	% of ori-	% in	% of	% in	% of
	residue:	ginal	residue:	original:	residue	original
	:	:lignin	:	:pentosan:	:	:cellulose
1 :	5.60 :	4.10 :	4.60 :	3.78 :	40.3 :	26.5
2 :	6.65 :	5.75 :	4.20 :	4.02 :	32.8 :	25.1
3 :	6.87 :	6.21 :	5.41 :	5.41 :	40.8 :	32.7
4 :	6.93 :	6.48 :	4.35 :	4.51 :	30.7 :	25.4
5 :	9.10 :	7.49 :	5.68 :	5.19 :	30.5 :	22.1
6 :	6.60 :	5.32 :	4.76 :	4.26 :	31.2 :	22.3

The per cents based on the original amount of constituent present in the stalk were calculated using the following values:

31 per cent lignin (free from ash) - determined with 72 per cent sulphuric acid.

28 per cent pentosan - determined by the phloroglucinol method.

35 per cent cellulose - Cross and Bevan cellulose corrected for pentosans.

A study of the results obtained in this series of experiments shows that the addition of the V_2O_5 as a catalyst increases the yield of oxalic acid only under two conditions:

(1) When the mixture of cobs and acid are not heated.

(2) When the mixture of cobs and acid are heated to the boiling point for a few minutes and then the reaction is checked by suddenly cooling the reaction flask and contents.

The nitric acid used alone gives greater yields under the following conditions:

(1) When a short heating period is employed not follow-

ed by sudden cooling.

(2) When long heating periods are employed.

The yields of residue are about the same whether a catalyst is used or not. The analyses of the residues indicate that the lignin, pentosan and alpha-cellulose contents of the residues are practically the same whether a catalyst is used or not. These results seem to indicate that the mechanism of the reaction is somewhat as follows; the larger portion of the lignins and pentosans originally present are rapidly resolved by the nitric acid and the cellulose is also rapidly and greatly affected by the acid but not to such a great extent as the other two constituents. The resolution of these constituents bring about the formation of various intermediate degradation products, a considerable portion being oxalic acid. After the nitric acid has brought about the resolution of these constituents the catalyst (V_2O_5) goes to work on the intermediate compounds and produces from these intermediates an increased yield of oxalic acid. This beneficial effect of the catalyst takes place if the reaction mixture is kept cool, but if the temperature is increased up to or near the boiling point the effect of the catalyst is to cause further oxidation of the oxalic acid already formed to the ultimate end products, carbon dioxide and water. Also, when the temperature is high, the catalyst, instead of oxidizing the intermediate products to oxalic acid, hastens their oxidation through this stage on to the ultimate end products, carbon di-

oxide and water. This is indicated both by the yields of oxalic acid, and by the vigorous gassing during the unchecked catalytic reaction.

On the other hand, the catalyst does not seem to be able to cause the resolution of any more of the original raw material than the nitric acid when used alone can resolve. Therefore the original break down of the material depends on the strength and amount of nitric acid used, whereas the catalyst influences the production of oxalic acid from the intermediates formed originally by the nitric acid but has no influence on material that is not in solution.

Increased yields of oxalic acid result from prolonged heating when nitric acid is used alone and there is no decomposition of the oxalic acid formed by the nitric acid. But if the catalyst (V_2O_5) is present the procedure should be as follows; the mixture is heated at the boiling point of the acid for a few moments to assist the nitric acid in dissolving the material. Then after a few moments of boiling, the mixture should be cooled and kept cooled so that the catalyst can assist in the formation of oxalic acid from the compounds in solution. If the mixture is not cooled the catalyst destroys the oxalic acid already formed, and also causes any oxalic acid that may be formed later to be oxidized to simpler compounds, such as carbon dioxide and water.

Increasing the nitric acid to cob ratio from 6:1 to 12:1 is beneficial when nitric acid is used alone and the heat-

ing period is prolonged, or when the catalyst is used and there is no heating, or a short heating period followed by sudden cooling. It was shown previously that it was cheaper to use 55 per cent nitric acid in 6:1 ratio if a 55 per cent yield of oxalic acid was obtained than to use 1.5 sp. gr. nitric acid in 5:1 ratio when a 100 per cent yield of oxalic acid was obtained. The yields of oxalic acid in this series, when a 6:1 acid ratio and no catalyst were used, were not as high as those obtained in the series of experiments recorded in the previous section, but when a 12:1 ratio was used such as in run #11 a yield of 64.6 per cent oxalic acid was obtained which is fairly close to the 70 per cent yield that would be necessary in order to make the 60 per cent acid cheaper to use than the 1.5 sp. gr. nitric acid.

The residues left from the oxidations with 60 per cent nitric acid did not seem very promising. The alpha-cellulose contents were only about 50 per cent, and the residues also had the appearance of being gelatinized to some extent. When dried at 105° C they formed hard, horny masses which were very difficult to grind up for analysis. They also had a slightly yellow tinge after being dried. Since the alpha-cellulose content was low they evidently consisted mostly of oxy-cellulose, and other degraded celluloses.

3. Effect of Various Catalysts Added to the Filtrate:

a. 200 grams of ground cobs were mixed with 800 grams of 40 per cent nitric acid in a two-liter balloon flask fitted with a reflux condenser and the mixture was digested at the boiling point for one hour. The mixture was allowed to stand without further heating for four hours. It was then filtered and the residue was washed, oven dried and weighed. The oven dry residue weighed 60 grams.

The filtrate and wash water were combined and made up to two liters with distilled water. Several 200 c.c. portions of this liquid were measured out into Erlenmeyer flasks and placed on a hot plate. Catalysts were added and the liquids were allowed to stand for 48 hours at 40°C. Make-up water was added at intervals. The contents of the several flasks were then analysed for oxalic acid. The results are given in the following table.

No.	Catalyst Used	Grams Oxalic Acid in the 200 c.c. Portion	Yield Oxalic Acid Based on Air Dry Cobs
1	Vanadic oxide	3.59	17.95
2	Chromic oxide	3.26	16.3
3	Titanic oxide	3.84	19.2
4	Molybdic oxide	3.70	18.5
5	Tungstic oxide	3.64	19.2
6	None	3.46	17.3

b. 100 grams of cobs were treated with 640 grams of 40 per cent nitric acid in a manner similar to series #1 except the boiling period was 1 1/2 hours and the mixture was allowed to

stand without further heating for three days. It was then filtered and the residue was washed. The filtrate and washings combined were made up to one liter with distilled water. Several 100 c.c. portions were measured into Erlenmeyer flasks and allowed to stand two days in the presence of various catalysts. The results are given in the following table.

No.	Catalyst Used	Grams Oxalic acid in the 100 c.c. Portion	% Yield Oxalic Acid Based on Air Dry Subs
1	Vanadium pentoxide:	3.15	51.5
2	Vanadium pentoxide: Molybdic acid	3.55	35.5
3	Tungstic acid	3.06	50.8
4	Titanic acid	2.93	29.5
5	No catalyst	2.99	29.9
6	No catalyst	3.02	30.2

4. Effect of Length of Heating Period in Presence of

Catalyst: In this series of experiments 50 gram portions of ground cobs were digested with 520 grams of 40 per cent nitric acid for various periods at the boiling point. The reaction mixtures were then allowed to stand without further heating for three days. They were then filtered and the residues washed. The combined filtrate and washings were made up to one liter and analyzed for oxalic acid. The results were as follows.

No.	: Heating Period :	: Catalyst :	: Yield Oxalic :
	: in Hours :		: Acid Based on Air :
	:		: Dry Cobs :
1	: 1 :	V_2O_5	: 56.2
2	: 1 1/2 :	"	: 35.5
3	: 2 :	"	: 28.6
4	: 3 :	"	: 25.8

It seemed evident from these results that the yield of oxalic acid was decreased by continued heating so a series of experiments were carried out to determine the stability of oxalic acid in nitric acid of various strengths and temperatures.

5. Stability of Oxalic Acid in Nitric Acid Solutions:

Crystals of C. P. oxalic acid were used in the following experiments. The crystals were ground to a fine powder and then kept in a stoppered bottle. For each determination a two gram sample was weighed out and dissolved in 100 c.c. of nitric acid.

A ten c.c. portion of this was pipetted out and the oxalic acid content determined by titration with standard potassium permanganate solution. The oxalic acid content was determined at the beginning of each run and again after a period of three hours.

The nitric acid and dissolved oxalic acid were transferred to large test tubes, supported by a rack, and held at the desired temperature for three hours. Two samples for each temperature and concentration of acid were used. To one of these 0.1 gram of vanadium pentoxide was added, while the other contained no catalyst. For the runs at temperatures above 40°C. the level of the liquid in the test tubes was kept constant by adding water at intervals. At the end of the heating period the samples were cooled, shaken well and then analyzed for oxalic acid. The results were as follows.

The data are given as grams remaining in solution.

No.:	Heating	Strength:						
:	Period	EMO %	20°C	40°C	60°C	75°C	90°C	
:	in Hours:	3	:	:	:	:	:	:
1	3	17	2	1.98	1.99	1.98	1.82	
2	3 (c)	17	1.98	1.97	1.86	1.67	0	
3	3	32	1.99	1.99	1.99	1.97	1.81	
4	3 (c)	32	1.98	1.88	1.93	1.76	0	

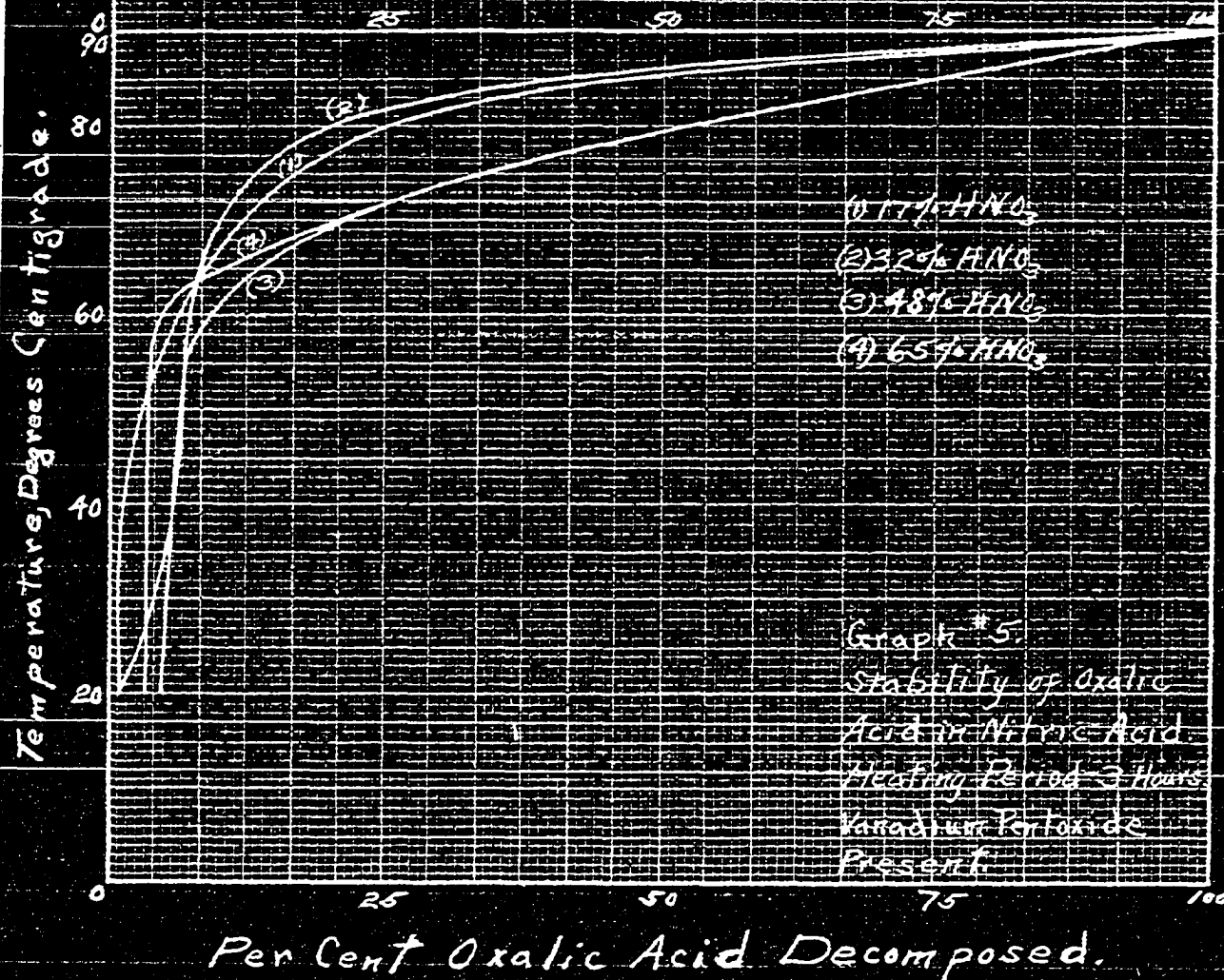
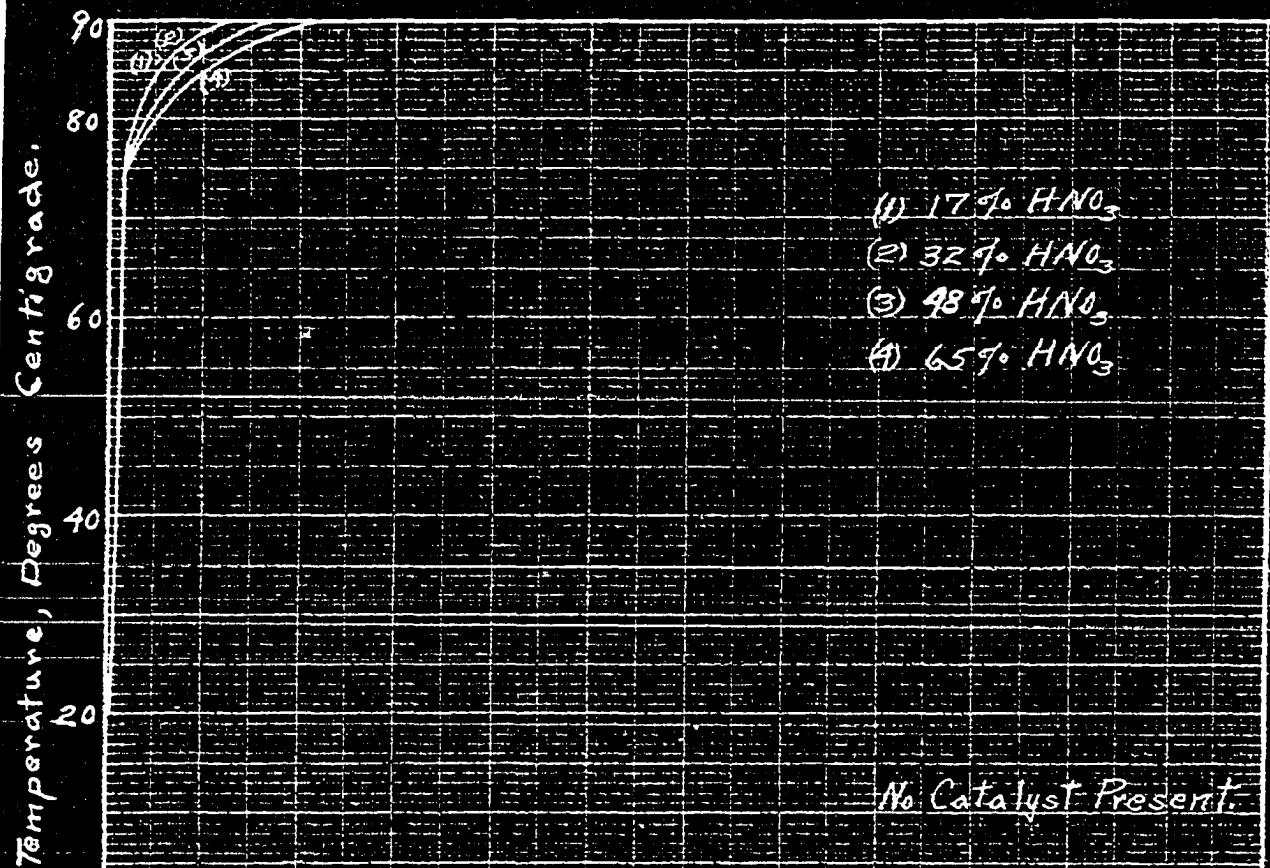
(c) indicates the use of vanadium pentoxide.

No.	: Heating : Period : in Hours	: Strength : HNO ₃ % : 5	: 20°C	: 40°C	: 60°C	: 75°C	: 90°C
5	: 3	: 48	: 2	: 1.96	: 1.99	: 1.99	: 1.74
6	: 3(c)	: 48	: 1.89	: 1.96	: 1.91	: 1.34	: 0
7	: 3	: 65	: 2	: 1.97	: 1.99	: 1.92	: 1.63
8	: 3(c)	: 65	: 1.94	: 1.96	: 1.95	: 1.37	: 0

The results given in the table are shown graphically in figure # 5 which brings out in a striking manner how rapidly oxalic acid is decomposed by nitric acid in the presence of vanadium pentoxide.

The curves in figure # 5 show that up to temperatures of 60°C the effect of the nitric acid on the oxalic acid is rather small in all cases. Above 60°C the decomposition increases as the concentration of the nitric acid increases. This decomposition is so accelerated by vanadium pentoxide that when it is present the oxalic acid is entirely destroyed by all concentrations of nitric acid used in the experiments at a temperature of 90°C.

These results explain very clearly why the yields of oxalic acid from cobs by digestion with nitric acids of concentrations less than 70 per cent are scarcely affected by the time of heating when no catalyst is present. In these cases the yield is usually increased slightly, the decomposition of the cobs being somewhat faster than the decomposition of the oxalic acid formed. The reverse is true, however, when vanadium



pentoxide is present. The results indicate that the decomposition of the oxalic acid formed is faster at high temperatures than the decomposition of the more resistant parts of the cob to form oxalic acid. This reversal of formation of oxalic acid seems to take place after about one hour at the boiling temperature when 40 per cent nitric acid is used. With stronger acids it probably takes place somewhat sooner and with weaker acids somewhat later. This would depend on the speed of formation of the oxalic acid as the rate of decomposition is quite rapid at 90⁰ C for all strengths of nitric acid between 17 and 65 per cent as far as investigated.

6. Successive Treatment of Corn Cobs with Increasing Strengths of Nitric Acid: Several experiments were carried out in which the cobs were first treated with a relatively weak nitric acid. The residues of pulp from these treatments were then treated with stronger nitric acid. The residues from these treatments were treated with a still stronger acid and in this manner the treatments were carried through four stages.

The reasons for these successive treatments were as follows. It is known that lignins, which comprise about 35 per cent of the cob, are very susceptible to treatment with nitric acid. This action is due not so much to the hydrolyzing power of the acid, since lignin is quite resistant to fuming hydrochloric acid and strong sulphuric acid, but to the oxidizing power of nitric acid. One of the characteristic properties of lignin is the ease with which it is decomposed by oxidizing agents. The chief products of the reaction aside from carbon dioxide and water are the simple aliphatic acids. Another important constituent of the cob is xylan which comprises about 25 per cent. Xylan is easily hydrolyzed to xylose with dilute nitric acid and treatment with stronger nitric acid resolves xylan into oxalic acid and other oxidation end products. Cellulose, the third important constituent of the cob, is more resistant to resolution with nitric acid than are lignin and xylan. It was thought that by treating the cob with a relatively weak nitric acid the lignin and xylan would be oxidized to oxalic

and other simple aliphatic acids without a very drastic treatment. This portion would then be separated from the residue of cellulose and degraded celluloses so that any oxalic acid which had formed would not be destroyed by continued treatment with the nitric acid. The cellulosic residue would then in turn be treated with a stronger nitric acid, the soluble products removed as before, and this treatment continued until ultimately all the cob had been decomposed. It was hoped that in this way the oxalic acid formed at different stages would be preserved to the greatest possible degree.

Another factor considered was the economy of the process. By securing as high oxalic acid yields as possible with dilute nitric acids the cost of production would be considerably reduced. The more resistant residues which demand stronger acid could then be treated with smaller ratios of strong nitric acid than if the ratio was based on the original weight of the cob.

This method of treatment would require somewhat more handling than a single treatment but it is believed that a satisfactory counter-current process can be devised which would reduce handling to a minimum. However, without any data on which to base this conclusion, it is thought that the total yield of oxalic acid would have to be materially higher than that resulting from a single treatment to compensate for the increased handling cost.

In the following experiments all the treatments were carried out in round-bottomed balloon flasks fitted with reflux

condensers. The flasks were heated with gas burners. The first treatments were carried out in two-liter flasks and for succeeding treatments smaller flasks were used as the residues became smaller. The procedures are first given in detail and then a summary of results is given in tabulated form.

Experiment #1.

A. 200 grams of cobs ground to 20 mesh were mixed with 1200 grams of 15 per cent nitric acid. The mixture was heated gradually to the boiling point of the acid. The heat was then removed and the mixture was filtered at once on a Buchner funnel through a woolen cloth. A suction flask was used. The residue was washed free of nitric acid with hot water, the filtrate and washings being kept separate. They were allowed to stand for a week before being analyzed for oxalic acid. The washings showed practically no oxalic acid. The total oxalic acid in both filtrate and washings was 9.84 grams. The washed residue was dried at 105°C and then weighed. The residue weighed 118 grams.

B. The residue (118 grams) from A was treated with six times its weight (708 grams) of 30 per cent nitric acid. The mixture was heated to the boiling point of the acid. Heating was then discontinued and the mixture was filtered at once. The procedure from then on was identical with that of A. The oxalic yield was 8.05 grams. The weight of the oven-dry residue was 80 grams.

C. The residue (80 grams) from B was treated with five

times its weight of 45 per cent nitric acid. The acid was heated to the boiling point, then the mixture was filtered and the filtrate and residue were treated in the same manner as A and B. The oxalic acid yield was 5.68 grams. The oven-dry residue weighed 58 grams.

D. The residue (58 grams) from C was treated with five times its weight (290 grams) of 60 per cent nitric acid and the same procedure carried out as for A, B and C. The yield of oxalic acid was 7.60 grams. The oven-dry residue, which was a finely pulped white mass, weighed 20 grams.

Experiment #2.

Each stage in this experiment was carried out in the same manner as in Experiment #1 except that the heating was continued in each case for thirty minutes after boiling commenced. The filtrate and washings were allowed to stand separately for a week before being analyzed for their oxalic acid content.

A. 200 grams of ground cobs were treated with 1200 grams of 15 per cent nitric acid. The yield of oxalic acid was 13.45 grams. The oven-dry residue weighed 100 grams.

B. The 100 grams of residue from A were treated with 600 grams of 50 per cent nitric acid. The yield of oxalic acid was 7.42 grams. The oven-dry residue weighed 67 grams.

C. The residue (67 grams) from B was treated with five times its weight (335 grams) of 45 per cent nitric acid. The oxalic acid yield was 5.38 grams and the oven-dry residue weighed

ed 50 grams.

D. The 50 grams of residue from C were treated with five times its weight (250 grams) of 60 per cent nitric acid. The oxalic acid yield was 4.10 grams and the oven-dry residue weighed 17 grams.

The results of the two foregoing experiments are given in the following table.

No.:	Material Used	:Grams :Residue:	:Oxalic Acid Yield: :In % of:	:Nitric :Acid Used :(As 100%)
			:Grams:Air :Resi- :Dry :due :Acid) :Cobs: :Grams	
	:200 gms. cobs (air dry):	:	:	:
1A	:1200 " 15% HNO ₃	: 118	: 9.64:4.92:	: 180
	:118 gms. residue	:	:	:
B	:708 " 30% HNO ₃	: 80	: 8.05:4.03: 6.82:	: 212.4
	:80 gms. residue	:	:	:
C	:400 gms. 45% HNO ₃	: 58	: 5.68:2.84: 7.11:	: 180
	:58 gms. residue	:	:	:
D	:290 " 60% HNO ₃	: 20	: 7.60:3.80:13.1	: 174
	:200 gms. cobs (air dry):	:	:	:
2A	:1200 " 15% HNO ₃	: 100	: 13.45:6.73:	: 180
	:100 gms. residue	:	:	:
B	:600 " 30% HNO ₃	: 67	: 7.42:3.71: 7.42:	: 180
	:67 gms. residue	:	:	:
C	:355 " 45% HNO ₃	: 50	: 5.38:2.69: 8.03:	: 151
	:50 gms. residue	:	:	:
D	:250 " 60% HNO ₃	: 17	: 4.10:2.05: 8.2	: 150

The total yield of oxalic acid and the total amount of nitric acid (as 100 per cent) used is shown in the following table.

No.	Total Oxalic Acid Yield In Grams	% of Air-dry cobs (as 100%)	Total HNO ₃ Used Grams	Ratio Acid:Cobs
1	31.17	15.58	746.4	3.73
2	30.35	15.18	661	3.50

A comparison of the results of Experiment 2 with those obtained using a single treatment of 55 per cent nitric acid is given below.

Method	% Yield Oxalic Acid	Ratio Acid:Cobs (as 100% HNO ₃)	HNO ₃ Used (as 100%) per 100 gms. air-dry cobs
Single	35	6.0	600
Successive (#2)	15.18	3.3	330

Hence to secure the same amount of oxalic acid by the successive method as in the single treatment with 55 per cent nitric acid would require somewhat more nitric acid (as 100 per cent) and cobs. This increased cost added to the increased handling cost due to the several treatments makes the successive method of decomposing cobs to oxalic acid less attractive commercially than the single treatment method using a strong nitric acid (50-60 per cent).

C. Treatment of Corn Cobs With 10-20
Per Cent Nitric Acid

This phase of the work was concerned with the production of oxalic acid from corn cobs using nitric acid of strengths ranging from 10 to 20 per cent. In all cases the cobs were ground to about 20 mesh in a sample mill. The digestion of the cobs with the acids were carried out in one liter balloon flasks fitted with reflux condensers. After the mixtures were digested at boiling temperatures for the required time the products were allowed to stand from 36 to 48 hours before being filtered. They were then filtered on Buchner funnels using woolen filter cloths and the residues were washed with hot water until free from nitric acid. The filtrates were then analyzed for their oxalic acid contents. The results of the experiments are shown in the following table.

No.	Strength HNO ₃ %	Grams HNO ₃	Grams Cobs	Heating Period : Hours	Yield % Oxalic Acid : Air-dry basis:	Remarks
1	10	250	20	1	1.85	No catalyst
2	"	"	"	2	1.95	" "
3	"	"	"	3	2.13	" "
4	"	"	"	1	2.96	V ₂ O ₅ catalyst
5	"	"	"	2	3.06	" "
6	"	"	"	3	3.33	" "
7	"	"	"	1	3.25	V ₂ O ₅ , H ₂ O ₂
8	"	"	"	2	2.96	" "
9	"	"	"	3	3.52	" "
10	15	"	"	1	2.23	No catalyst
11	"	"	"	2	2.61	" "
12	"	"	"	3	2.78	" "
13	"	"	"	1	3.10	V ₂ O ₅ catalyst
14	"	"	"	2	3.30	" "
15	"	"	"	3	3.25	" "

No.	Strength: HNO ₃ %	Grams: HNO ₃	Grams: Cobs	Heating: Period :Hours	Yield % Oxalic acid :air-dry basis:	Remarks
16	15	250	20	1	3.21	V ₂ O ₅ , WO ₃
17	"	"	"	2	2.96	" "
18	"	"	"	3	3.72	" "
19	20	"	"	1	2.52	No catalyst
20	"	"	"	2	2.14	" "
21	"	"	"	3	2.97	" "
22	"	"	"	1	3.20	V ₂ O ₅ catalyst
23	"	"	"	2	3.26	" "
24	"	"	"	3	3.41	" "
25	"	"	"	1	3.55	V ₂ O ₅ , WO ₃
26	"	"	"	2	3.47	" "
27	"	"	"	3	3.29	" "

The foregoing results indicate that nitric acid of the strengths used do not give a promising yield of oxalic acid. The yields in all cases were very low even when long heating periods and very active catalysts were employed. The yields using nitric acid of a certain initial strength vary but slightly with the heating period. A slight increase in oxalic acid yield is noted as the strength of the nitric acid is increased and the presence of catalysts also increase the yields to some extent.

It is evident that, although the nitric acid decomposes the cobs to some extent, the treatment is not drastic enough to cause much resolution of the components of the cob to oxalic acid and other end products.

The residues of pulp from these experiments are of more interest than the yields of oxalic acid secured. The

residues from the foregoing runs were not studied at the time but some pulps secured in a similar manner using 10 per cent nitric acid were studied later as to their chemical compositions and the results of these studies are given in Part II of this thesis.

It is proper at this stage of the problem to introduce an abstract of some very interesting work done by Baly and Chorley (18) on the action of nitric acid on the ligno-celluloses. In their work beech wood sawdust was treated with 10 per cent aqueous solutions of nitric acid. The ratio of the weight of nitric acid (as 100 per cent HNO_3) to the sawdust was 1:5 or 33 per cent. The mixtures of sawdust and nitric acid were heated in flasks on waterbaths for from four to five hours at the end of which periods the evolution of nitrous gases had ceased.

The gases evolved during a typical reaction were collected and analysed. The results were as follows:

<u>Gas</u>	<u>Per Cent by Volume</u>
H_2	18.3
H_2O	9.4
NO	9.3
NO_2	53.2
HCN	8.3
CO_2	17.2
CO	4.3

The NO and NO_2 given off represented 52.4 per cent by weight of the nitrogen in the nitric acid used.

Other products of the reaction were also analyzed. They were considered in four groups and the results were:

Product	% Yield (Based on Air-Dry Sawdust)
(a) Fibrous residue	48.00
(b) Volatile acids (Chiefly acetic)	11.80
(c) Oxalic acid	5.84
(d) Soluble derivatives of non-cellulose	26.16

The fibrous residue contained some oxycellulose and on distillation with hydrochloric acid (sp. gr. 1.06) yielded 4.5 per cent furfural. This may have come from pentosans present or the oxycellulose or from both, which is most probable.

The soluble derivatives, when evaporated down, gave a yellow gummy residue. Further oxidation with nitric acid gave oxalic acid, volatile acids and oxides of carbon.

Baly and Chorley as a result of their researches arrived at the following conclusions:

(1) The first groups to be attacked are the keto-R-hexene molecules of the ligno-cellulose. These undergo destructive oxidation.

(2) The more easily hydrolysable groups (pentosans and beta-celluloses) are next attacked and are dissolved with more or less attendant oxidation, according to the duration of temperature of the reactions.

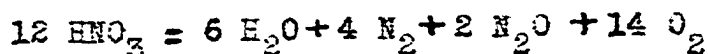
(3) The cellulose is attacked to a slight extent and some of it is converted to oxycellulose.

They regard ligno-cellulose as -

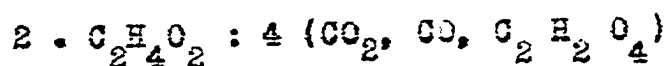
	Non-cellulose	
$4 \cdot \text{C}_6\text{H}_{10}\text{O}_5$ Cellulose	$\text{C}_5\text{H}_{10}\text{O}_5$ Pentosans	$\text{C}_{19}\text{H}_{18}\text{O}_8$ Containing one keto-R-hexene group

Taking into account only the HNO_3 deoxidized to $\text{H}_2\text{O} + \text{N}_2$, the molecular ratio is 6 HNO_3 . The reaction is thought to take place by the oxidation of the one keto-hexene group of the non-cellulose complex; the acetic acid being formed partly from this group, with CH_3 residues obtained from groups in combination.

The nitric acid is broken down as below:



Taking an approximate formula, $\text{C}_6\text{H}_6\text{O}_3$, for the hexene group, and allowing for the destructive oxidation of the C_6 nucleus, with the attendant union of COOH to CH_3 , the molecular proportion of the characteristic products is -



that is, of the six carbons, two are split off as acetic acid; the remainder are similarly oxidized, and after oxidation two are liberated in the simpler forms and two remain in the residual solution.

The remaining groups of the complex ligno-cellulose formulated above are resolved as follows:

The cellulose is separated insoluble in the approximate ratio $4\text{C}_6\text{H}_{10}\text{O}_5$, but containing some oxy-cellulose; the

pentosan is dissolved, and the residues of the lignone complex are also hydrolysed and dissolved.

It is evident that dilute nitric acids do not give a high enough yield of oxalic acid to be used commercially. However the acetic acid formed increases the value of the products to a point commensurate to the nitric acid loss. An approximate calculation will illustrate this fact. The market price of 28 per cent acetic acid is about 4 cents per pound, that of oxalic acid is about 11 cents per pound. Therefore the value of the products per 100 pounds of cobs used would be approximately (using the results of Baly and Chorley as an example):

$$3.84\% \text{ oxalic acid } \times .11 = \$0.42$$

$$12\% \text{ acetic acid } \times .14 = \underline{1.68}$$

$$\text{Total} = 2.10 \quad \text{Value} = \$2.10$$

$$\text{Nitric acid/100\% cobs} = 33\%$$

$$\text{Nitric acid loss} = 50 \text{ per cent} = 16\%$$

$$\text{Cost of nitric acid lost, } 16 \times .05 = \$0.80$$

(5 cents per pound)

$$\text{Cost of recovering the other } 16\% = \underline{0.08}$$

(estimated at 1/2 cent per pound for recovering as 60% HNO_3)

$$\text{Total} = 0.88$$

$$\text{Cost} = \underline{0.88}$$

$$\text{Gross profit} = 1.22$$

If the cost of recovering the oxalic and acetic acids was not too great it would seem that there is a possibility of using dilute nitric acid. Furthermore the pulp residue from

this treatment has interesting possibilities as a source of cellulose, and it is probable that if dilute nitric acid is used, the cellulose residue will be the principal product while the oxalic and acetic acids will be worked up as by-products.

An investigation is under way at present to determine the yields of acetic acid obtained from corn stalks and cobs using the process of Baly and Chorley. Their method of analyzing the filtrate for volatile acids was to add iron filings to reduce the nitric acid and then to distill off the volatile acids using sulphuric acid.

When this method was tried, using the acid filtrate from a corn stalk digestion, it was found that some nitric acid was usually present in the distillate. The presence of nitric acid was detected using ferrous sulphate and sulphuric acid. In one case, however, no nitric acid was present, and the yield of volatile acids, based on the air dry weight of the stalks, was about 9 per cent. When some of this distillate was digested with mercuric oxide and then redistilled and titrated, it was found that about one-half of the volatile acids had been destroyed and the yield of acetic acid was about 5 per cent. The volatile acids destroyed were probably mostly formic acid, which is decomposed by digestion with an excess of mercuric oxide.

Further studies are being made on this problem by L. Kuhn and the author, and the results will be given in Kuhn's departmental thesis.

D. Formation of Other Aliphatic Acids

As is known, the carbohydrates when completely oxidized are converted to carbon dioxide and water. Partial oxidation, however, brings about the formation of many compounds depending upon the conditions of the oxidation and the primary material. Among the intermediate products formed are various acids such as gluconic, glucuronic, saccharic, mucic, tartaric, humic and many others. On further oxidation these are converted to oxalic acid with the simultaneous production of some carbon dioxide and water.

With the exception of tartaric acid, none of these intermediate products are of much commercial value, and no studies were made of their formation during the process of obtaining oxalic acid from corn stalks and cobs.

It has been suggested that some of these "aldonic" acids are suitable for making sour drinks similar to lemonade and G. Beal in a departmental thesis has studied the conditions of the formation and extraction of some of these acids.

E. Procedure to Obtain High Yields of Oxalic Acid.

In the foregoing text the statement is often made that a yield of one pound of oxalic acid from one pound of cobs is the best result that has been obtained experimentally. This yield has been obtained by Trexel (4) and by Webber (5) using 95-100 per cent nitric acid, in the proportion of five parts of acid to one part of cobs, and a catalyst such as vanadium pentoxide.

It is suggested that for consistent high yields of oxalic acid the following procedure be used: Dissolve the cobs in a low ratio (3:1 to 5:1) of 1.5 sp. gr. nitric acid by gentle heating, preferably on a water bath. Then cool the mixture, and add a very small amount of vanadium pentoxide (V_2O_5) and some 70 per cent (1.42 sp. gr.) nitric acid. The amount of this acid added should be about two or three times the initial weight of the cobs. Keep the mixture cooled for two or three days so that there will be ample time for oxalic acid formation.

The object of this procedure is to get the cobs entirely into solution at a fast rate by the use of strong acid and moderate heating. The heating period in the presence of the very strong acid should not be very long or some oxalic acid may be destroyed. Then when the cobs are in solution, vanadium pentoxide (V_2O_5) is added to the cooled solution as its presence greatly increases the yield of oxalic acid. Modi-

fications of this procedure can be used, but two precautions should always be observed, namely; do not dilute the solution with water for two or three days, and do not heat the solution after the vanadium pentoxide has been added. Consistent yields of about 100 per cent can be easily obtained in the foregoing manner, and the process is easy to control at all stages.

Some examples are given in the following table:

Cobs	:1.5 sp. gr. HNO_3		: 70% HNO_3		:Yield oxalic acid	
Gms.	: Gms. :	Ratio	:Gms. :	Ratio	: Gms. :	% (air dry
	:	acid	:	acid	:	:cobs)
	:	cobs	:	cobs	:	:
10	: 30 :	3:1	: 30 :	3:1	: 9.4 :	94%
10	: 40 :	4:1	: 20 :	2:1	: 9.3 :	93%
10	: 50 :	5:1	: 20 :	2:1	: 9.7 :	97%
10	: 50 :	5:1	: 0 :	-	: 8.9 :	89%

IV - SUMMARY

OXIDATION WITH NITRIC ACID

The results of the experimental work done on the oxidation of corn cobs with nitric acid to produce oxalic acid can be summarized as follows:

(1) Pretreatment of the cobs with nitrous oxides is beneficial, but oxidation of the cobs to oxalic acid can not be accomplished by the nitrous oxides alone.

(2) The nitrous oxides evolved in this process are rich in NO_2 , and should be recovered with minimum tower space and high efficiency. It is probable that the nitrous oxides can be recovered as 55-60 per cent nitric acid.

(3) When strong nitric acids are used there should be very little loss of nitrogen as nitrous oxide (N_2O) or N_2 .

(4) Yields of oxalic acid greater than 100 per cent, based on the weight of the cobs, should be secured if possible before the process is attempted commercially. This applies when 1.5 sp. gr. (fuming) nitric acid is used in the optimum ratio of five parts of acid to one part of cobs.

(5) Nitric acids of from 50-70 per cent strength give much lower yields of oxalic acid, but economic factors would seem to make their use more feasible commercially than the use of 1.5 sp. gr. (fuming) nitric acid.

(6) The yields of oxalic acid secured with 50-70 per cent nitric acids indicate that the expensive step of nitric acid concentration (to 95-100 per cent acid) can be eliminated

from the cyclic process.

(7) Recovery of the nitrous gases as 60 per cent nitric acid from a water absorption system seems preferable to gassing reaction mixtures of cob and acid with the nitrous gases evolved from other similar retorts.

(8) When nitric acids of from 50-70 per cent strength are used two alternative procedures are possible to secure good yields:

(a) Boiling the mixture of cobs and acid for about an hour with no catalyst (V_2O_5) present.

(b) Boiling the mixture for a few minutes (5-6) in the presence of a catalyst (V_2O_5), then cooling the mixture immediately, and keeping it cool for two or three days.

(9) Oxalic acid in nitric acid solutions is rapidly destroyed at elevated temperatures ($90-100^{\circ} C$) in the presence of vanadium pentoxide (V_2O_5).

(10) Nitric acid rapidly decomposes the lignins and pentosans in the cobs and attacks the cellulose vigorously with the production of oxycellulose, other degraded celluloses, and soluble products. The extent of the resolution depends on the strength of the nitric acid used, and the time and temperature of the reaction period.

(11) The cellulose remaining unoxidized or insoluble is gelatinized to some extent and dries to a hard, horny mass, when strong nitric acids are used.

(12) The catalyst (V_2O_5) does not assist in the dis-

solution of the cobs, but has great effect on the soluble products formed by the action of the nitric acid on the cobs.

(13) Dilute nitric acid gives a low yield of oxalic acid, but offers a possible means of obtaining acetic acid and cellulose pulps from cobs and stalks.

V - PREVIOUS WORK

FUSION WITH ALKALI HYDROXIDES

Previous investigators discovered that woods when heated to high temperatures in the presence of the caustic alkalis were oxidized to acetic, formic, and oxalic acids. Gay-Lussac (19) in 1829 was the first to discover the formation of oxalic acid by fusing carbohydrates with alkalies. He obtained the acid by fusing sugar, sawdust, and cellulose with potassium hydroxide but he stated that sodium hydroxide could also be used although the yields were not as high as with potassium hydroxide.

Dale (20) started the commercial production of oxalic acid in England in 1856 using a mixture of sodium and potassium hydroxides and sawdust. His procedure was to mix the sawdust with a strong caustic solution in iron pans, and then heat the mixture to a temperature of from 200^o-250^o C. At this point the mass took on a lemon yellow color. The temperature was allowed to drop and the fused mass was dissolved in hot water. The solution was filtered and the filtrate treated with lime to give the calcium salt of oxalic acid. The precipitate of calcium oxalate was then treated with sulphuric acid giving calcium sulphate and free oxalic acid. The product was obtained by filtering off the calcium sulphate and crystallizing the oxalic acid from the filtrate. This commercial procedure endured for many years and was still being carried on in the early part of

the twentieth century but it finally had to yield to economic pressure exerted by the Goldschmidt process.

Possoz (21) in France in 1858 found that equal parts of potassium and sodium hydroxide could be used, but that sodium hydroxide could not be used alone. He obtained seventy parts of oxalic acid by fusing one hundred parts of sawdust and three hundred parts of potassium hydroxide.

Thorn (22) in Germany in 1875 carried on a very extensive investigation of this method of preparing oxalic acid. In one series of experiments one part of pine sawdust was added to a quantity of soda lye containing two parts of sodium hydroxide; in another series four parts of sodium hydroxide were taken. The following were the results obtained:

50 grams of sawdust with 100 grams of sodium hydroxide fused in an iron pot:

At 200°C the yield of oxalic acid was 56 per cent.

At 220°C " " " " " 53.2 " " .

When the mixture was heated in a thin layer:

At 200°C the yield of oxalic acid was 34.68 per cent.

At 220°C " " " " " 31.60 " " .

25 grams of sawdust with 100 grams of sodium hydroxide fused in an iron pot:

At 240°C the yield of oxalic acid was 42.80 per cent.

In thin layers:

At 240°C the yield of oxalic acid was 52.14 per cent.

The color of the melt passed from brown to a bright yellow; above 180°C the mass assumed a green or brownish green color; at still higher temperatures a vapor with a disagreeable odor was evolved indicating that a considerable decomposition was taking place. The heating above 200° required great care to prevent the temperature from rising too high and causing the decomposition of the oxalic acid formed. This was especially true when the two to one ratio of caustic to sawdust was used.

Thorn obtained the following results when a mixture of potassium and sodium hydroxides and sawdust was fused in an iron pot:

Parts KOH	Parts NaOH	Parts Sawdust	Temp. $^{\circ}\text{C}$	No. of Experiments	Oxalic Acid Per Cent Yield
20	80	50	190	2	19.78
20	80	50	200	1	21.50
20	80	50	240	2	30.04
30	70	50	190	3	21.58
30	70	50	240	4	38.89
40	60	50	190	1	14.00
40	60	50	200	5	30.55
40	60	50	240-245	4	43.70
50	50	50	200	2	25.76
50	50	50	240-245	4	39.04
60	40	50	200	3	30.57
60	40	50	240-245	4	42.67
80	20	50	200-220	4	45.59
80	20	50	240	3	61.32
90	10	50	240	2	64.24
100	0	50	240-245	3	65.51

When the mixtures were heated in thin layers on an iron plate results as follows were secured:

KOH	Parts : NaOH	Parts : Sawdust	Temp. C.	No. of Experiments	Oxalic Acid Per Cent Yield
0	: 100	: 50	: 200-220:	2	: 33.14
10	: 90	: 50	: 230 :	2	: 58.36
20	: 80	: 50	: 240-250:	4	: 74.76
30	: 70	: 50	: 240-250:	3	: 76.77
40	: 60	: 50	: 240-250:	6	: 80.57
60	: 40	: 50	: 240-250:	6	: 80.08
80	: 20	: 50	: 245 :	4	: 81.24
100	: 0	: 50	: 240-250:	6	: 81.23

Thorn ascribed these higher yields to the fact that the mixture was more exposed to surface oxidation but the use of air preheated to 100° to 120° C although it shortened the time required did not increase the yield. The optimum ratio of KOH:NaOH from the economical standpoint is evidently 40:60.

Preen (5) fused one part of sawdust with two parts of sodium hydroxide and obtained 35.2 per cent of oxalic acid at 200° C, and 50.0 per cent at 220° C. Fusion with four parts of alkali at 240° C increased the yield to 41 per cent.

Erdmann (23) in 1867 observed the formation of acetic acid by the fusion of wood with potassium hydroxide. Potassium hydroxide gave better yields than sodium hydroxide, and three parts of alkali to one of wood gave higher yields than a one to one ratio. He obtained the following yields using three parts of potassium hydroxide:

	at 150° C. Acetic Acid Per Cent	at 200-250 $^{\circ}$ C. Acetic Acid Per Cent
Cane Sugar	46.0	35
Hydrocellulose (from cotton)	19.5	29
Jute	15.0	37
Pine wood	18.0	28

Mahood and Cable (24) in 1919 at the Forest Products Laboratory made a very extensive investigation of the optimum conditions for the formation of formic and acetic acids by the caustic fusion of several species of woods. Their results using 1 1/2 parts and 2 parts of sodium hydroxide to 1 part of sawdust are given in the following table:

Species	: Hours	: Ratio	170°C.		250°C.		: Oxalic
			Total Volatiles	Acetic Acid	Total Volatiles	Acetic Acid	
			:tile Acid	:Acid	:tile Acid	:Acid	
			:Calc. as	:Per	:Calc. as	:Per	
			:Acetic Acid	:Cent	:Acetic Acid	:Cent	
			:Per Cent		:Per Cent		:Per Cent
White	: 3/4	: 1 1/2 : 1	: 12.2	: 4.9	: 12.5 ^a	: 11.2	: 20.0
Oak	: 1 1/2	: 1 1/2 : 1	: 14.4	: 5.2	: 12.2 ^a	: 7.7	: 26.9
	: 3	: 1 1/2 : 1	: 14.2	: 5.2	: 12.5 ^a	: 11.6	: 37.7
	: 6	: 1 1/2 : 1	: 15.5	: 5.4	: 23.6 ^b	: 12.2	: 40.3
	: 12	: 1 1/2 : 1	: 16.0	: 5.5	: 22.4 ^b	: 15.9	: 59.8
White	: 3/4	: 2 : 1	: -	: -	: 21.9 ^b	: -	: 38.9
Oak	: 1 1/2	: 2 : 1	: -	: -	: 6.1 ^a	: -	: 12.5
	: 3	: 2 : 1	: -	: -	: 21.4 ^b	: -	: 40.5
	: 6	: 2 : 1	: -	: -	: 14.1 ^a	: -	: 35.8
	: 12	: 2 : 1	: -	: -	: 8.9 ^a	: -	: 19.2

a - Charred.

b - Partially charred.

They found the above ratios of caustic to sawdust very unsatisfactory as only partial fusion resulted, the temperature was hard to control and the batch was very apt to char as a result of the heat generated by the exothermic reaction. Using 3 parts of caustic to 1 of sawdust better results were secured. The yields are given in the following table:

Organic Acids by Alkaline Fusion of Wood.
(Results in Per Cent - Ratio NaOH:Sawdust, 3:1)

Species	Time :Hours:	170°C.			:	200°C.		
		Total	Acetic	Oxalic		Total	Acetic	Oxalic
		:Volatile:	:	:		:Volatile:	:	:
		:Acid as :Acetic	:	:		:Acid as :Acetic	:	:
White Oak	3/4	9.5	4.1	6.6	:	14.7	5.9	12.5
(Quercus	1 1/2	9.5	4.3	5.6	:	17.7	7.1	19.6
alba)	3	15.9	6.4	24.1	:	26.2	10.2	31.5
	6	21.2	8.4	-	:	25.6	13.6	55.5
	12	30.5	11.4	38.0	:	21.6	15.6	62.5
	24	25.2	-	-	:	-	-	-
	48	27.4	-	-	:	-	-	-
Hard Maple	3/4	7.7	4.3	-	:	16.5	7.3	-
(Acer	1 1/2	8.0	4.7	-	:	22.6	10.0	24.9
saccharum)	3	9.6	5.3	-	:	27.5	12.8	46.4
	6	18.1	8.1	-	:	25.4	15.7	59.3
	12	16.0	7.2	-	:	32.2	16.3	-
Elm	3/4	10.2	6.7	-	:	17.7	9.9	-
(Ulmus	1 1/2	9.7	6.1	-	:	19.0	9.9	26.8
americana)	3	13.4	7.6	-	:	20.9	11.2	34.6
	6	15.8	8.6	-	:	27.9	14.4	73.6
	12	18.8	9.5	-	:	31.4	15.9	-
Longleaf	3/4	6.0	2.2	1.5	:	13.0	4.2	14.9
Pine	1 1/2	6.6	2.3	2.2	:	12.7	4.1	13.5
(Pinus	3	9.1	3.1	6.5	:	17.6	6.4	30.0
palustris)	6	24.0	8.4	57.2	:	17.4	14.4	70.0
	12	32.6	12.6	53.0	:	21.4	14.7	74.0

Species	Time :Hours:	230° C.			:	260° C.		
		Total	Acetic	Oxalic		Total	Acetic	Oxalic
		:Volatile:	:	:		:Volatile:	:	:
		:Acid as :Acetic	:	:		:Acid as :Acetic	:	:
White Oak	3/4	25.7	11.0	37.5	:	-	-	-
(Quercus	1 1/2	26.7	12.0	39.5	:	-	-	-
alba)	3	24.5	17.0	38.4	:	-	-	-
	6	20.6	17.6	33.3	:	-	-	-
	12	19.9	18.9	40.4	:	-	-	-
	24	-	-	-	:	-	-	-
	48	-	-	-	:	-	-	-
Hard Maple	3/4	22.0	11.5	-	:	-	-	-
(Acer	1 1/2	23.8	14.1	42.0	:	-	-	-
saccharum)	3	19.3	17.8	58.7	:	-	-	-
	6	21.0	18.1	46.4	:	-	-	-
	12	22.9	19.1	-	:	-	-	-

Species	Time :Hours:	250° C.			:	260° C.		
		Total	Acetic	Oxalic		Total	Acetic	Oxalic
		:Volatile:	:	:		:Volatile:	:	:
		:Acid as	:	:		:Acid as	:	:
		:Acetic	:	:		:Acetic	:	:
Elm	: 3/4:	23.6	: 12.8	: -	:	20.0	: 18.2	: -
(Ulmus	: 1 1/2 :	24.7	: 15.5	: 35.9	:	11.6 ^a	: 10.8 ^a	: -
Americana)	: 3 :	20.9	: 19.1	: 56.1	:	20.4	: 19.8	: 1.3
	: 6 :	24.9	: 18.7	: 50.6	:	22.2	: 21.2	: -
	: 12 :	21.1	: 18.5	: -	:	22.0	: 20.5	: -
Longleaf	: 3/4 :	19.5	: 7.9	: 48.6	:	-	: -	: -
Pine	: 1 1/2 :	22.0	: 9.4	: 54.6	:	-	: -	: -
(Pinus	: 3 :	18.4	: 12.0	: 58.9	:	-	: -	: -
palustris	: 6 :	16.4	: 14.0	: 69.5	:	-	: -	: -
	: 12 :	15.2	: 14.6	: 57.4	:	-	: -	: -

a - Ignited.

Mahood and Cable, from the results of their experimental work, arrived at the following conclusions: The yield of total volatile acid reaches a maximum at 170° C. and a twelve hour heating period with oak and pine, and at 200° C. for the same period with maple and elm. About 50 per cent or less of this acid is acetic or at these lower temperatures about equal parts of formic and acetic acids are obtained. The yield of acetic acid increases both with time and temperature up to 250° C. for a 5 - hour period so these are evidently the optimum conditions for the production of acetic acid. The maximum yield of acetic acid for these conditions was 19.1 per cent obtained from elm sawdust. The results on elm indicate that it is possible to shorten the heating period by raising the temperature to 260° C. but there is danger of igniting the batch. The yield of oxalic acid is highest for the longer periods of

heating at 200°C . At higher temperatures the yield decreases and at 260°C . most of the oxalate formed is decomposed. Pine gives a higher yield of oxalic acid and a lower yield of acetic acid than the hard woods.

The formation of oxalic acid appears to be independent of the acetic acid produced, but at least part of the formic acid formed is converted into oxalic acid at 200°C . and over as indicated by a decreasing percentage of total acid and increasing percentages of acetic and oxalic acids.

These two investigators also studied the formation of methanol and acetone from the fusion of sawdust and caustic by carrying out the reaction in an autoclave fitted with a condensing coil. About 2.5 per cent of methanol is formed during the process, 30 per cent of which is produced by simple hydrolysis while about 70 per cent results from the more drastic action involved in the fusion of the alkali and wood. The yield of acetone is almost negligible being only about 0.004 per cent.

A summary of their data shows that from 17-20 per cent of acetic acid can be obtained from hard wood sawdust by fusion with sodium hydroxide, while a yield of about 50 per cent of oxalic acid can be obtained. They obtained higher yields of oxalic acid with pine wood and caustic soda than Thorn did, and believed that yields approaching those obtained with caustic potash can be obtained by prolonged heating at 200°C . Their yields of acetic acid were lower than those obtained by Cross, Bevan, and Isaac using caustic potash. A ratio of three parts

of alkali to one part of sawdust was found to be most satisfactory.

Cash and Sayler (2) in 1922 investigated the possibilities of using corn cobs in place of wood sawdust in the fusion process. In their first experiment finely ground cobs were treated with a strong caustic solution containing both sodium and potassium hydroxides. The batch was heated to 240°C , in a shallow iron pan, in a gas muffle furnace. Foaming of the mass caused much trouble and it was difficult to secure good temperature control. The mass charred and poor results were secured. In the next few runs the batches were heated in large casseroles over a Bunsen burner. As the water was driven off more was added until the cobs were completely disintegrated. This resulted in black, slimy residues composed most of charred material. The results of the runs are given in the following table.

No.	Grams of Cobs	Grams of NaOH	Grams of KOH	Oxalic Acid Per Cent	Acetic Acid Per Cent
A	20	20	10	38.0	36.0
B	20	54	-	16.6	17.5
C	20	20	10	12.5	16.09
D	20	27	-	33.75	38.39
E	20	13	10	39.0	57.40

In another experiment 50 grams of cobs were treated with a caustic solution made by dissolving 75 grams of sodium hydroxide and fifty grams of potassium hydroxide in a small amount of water. The fusion was carried out in a casserole.

A yield of 37 per cent of oxalic acid and 19.92 per cent of acetic acid was obtained. Their final caustic run was made using 50 grams of cobs and 125 grams of sodium hydroxide. One tenth of a gram of vanadic acid was added as a catalyst. This batch was less sensitive to heat. It was heated strongly but no charring took place. The residue was a yellowish brown color. Their corrected results give a yield of 4.16 per cent of oxalic acid.

A lime fusion was tried. 50 grams of cobs were treated with 90 grams of lime and water was added to the mixture. After the lime slaked, heat was applied in an effort to get a fusion but the attempt was unsuccessful. The mass charred slightly but no fusion took place.

It will be noted that these investigators apparently secured high yields of acetic acid. It is believed that what they report is total volatile acid instead of acetic acid. Their method of analysis is given verbatim.

"Acetates of sodium and potassium are produced in the fusion. A 50 cc. sample of the solution is pipetted off and placed in a 500 c.c. distilling flask. To this 10 c.c. of phosphoric acid are added and the solution distilled to dryness. When the flask is cool 50 c.c. of water is added and the distillation is repeated. The distillate is titrated with standard sodium hydroxide solution. Care must be taken to avoid foaming during the distillation."

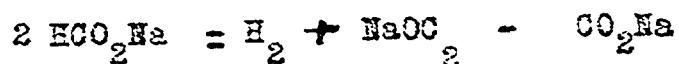
This method of analysis makes no differentiation between acetic and formic acid but gives the total yield of volatile acid which is made up almost entirely of the above two acids. It has been found by other investigators that in the case of woods under certain conditions of heating, etc., the yield of formic acid may equal or exceed the yield of acetic acid.

The action of fused sodium hydroxide on the three principal components of stalks and cobs, i. e., hemicelluloses, lignins, and cellulose, will be considered separately in order to gain an insight into the mechanism of the fusion process.

Heuser (26) believes that the action of fused alkali hydroxides on cellulose is a typical oxidation process. When cotton is slowly heated to 280°C. with four parts (by weight) of potassium hydroxide and seven parts (by volume) of water the reaction proceeds smoothly and hydrogen is evolved. When the evolution of hydrogen ceases the mass is taken up with water and the potassium oxalate is decomposed with dilute sulfuric acid. The oxalic acid can then be crystallized from the concentrated solution after removing the potassium sulfate. The yield is about 124 per cent. The three main products of the reaction are oxalic acid, acetic acid and hydrogen.

The hydrogen formation proves that an intermediate product is formed which, through splitting off of hydrogen, is transformed into oxalic acid. This is formic acid (or sodium or potassium formate). If this is heated, it splits off hydrogen

and yields oxalic acid:



This reaction is the basis of the formate method by which the bulk of oxalic acid is produced at the present time.

The formation of the formic acid is probably the result of an oxidation of the CH_2OH - and CHOH - groups of cellulose, through the aldehyde group to the carboxyl group. The fusion process, therefore, for cellulose takes place in two stages: the oxidation to formic acid, and the splitting off of hydrogen from the formic acid to form oxalic acid. The relative amounts of the acids formed depends on the conditions of the treatment.

Lignins, which comprise about one-third of corn stalks and cobs, represent the non-carbohydrate portion after the tissue has been freed from tannins, resins, fats, and similar secondary constituents. The structure of lignin is still uncertain but it is definitely established that lignin contains methoxyl, acetyl, and hydroxyl groups. The presence of ketonic and aldehydic groups has not been satisfactorily proved.

Lignin is very susceptible to oxidizing agents, and except in the case of alkali fusions, the products of the oxidation are the simple aliphatic acids, carbon dioxide and water. Lignin is rendered soluble by fusion (17) with alkalies. Heuser (17) states that no oxalic acid was formed by the fusion of carbohydrate-free lignin with caustic potash at temperatures

up to 270° C. It was later found that a 20 per cent yield of oxalic acid was obtainable when four parts of lignin were heated with 50 parts of caustic potash at 280° C. for 40 minutes. The alkaline fusion of lignin sulphonic acid gives vanillic or protocatechuic acid, catechol, acetic acid, and traces of higher fatty acids.

Lignin on fusion with potassium hydroxide in the presence of air gives protocatechuic acid (16 to 19 per cent), catechol (1 to 3 per cent), oxalic acid, and lignin acid. Below 240° C. the main product of the fusion is lignin acid. When the fusion is conducted in an atmosphere of hydrogen or nitrogen, the yield of oxalic acid is decreased and that of catechol is increased to 9 per cent. When iron is present in the melt, the yield of catechol is increased, while the protocatechuic acid is destroyed. Protocatechuic acid is believed to be an intermediate product in the formation of catechol.

Willstatter's lignin (isolated with fuming hydrochloric acid) on fusion with caustic potash gives formic acid but no oxalic or acetic acid (17). Catechol is not formed but traces of protocatechuic acid are produced.

The hemicelluloses or "wood gums" are composed mostly of pentosans. Xylan, one of the pentosans, constitutes about 27 per cent of corn stalks and cobs. When wood gum, obtained from beech-wood, is fused with caustic potash some succinic acid is formed but no catechol results. Straw xylan (17) fused

with 10 parts of caustic potash at 250° to 280° C. gives about 50 per cent oxalic acid, 13 to 15 per cent of acetic acid, and 8 to 12 per cent of formic acid. A slight amount of succinic acid is formed.

From the foregoing results, obtained using fairly pure samples of the several principal constituents of ligno-celluloses and pento-celluloses, the following deductions can be made.

(1) The oxalic acid is produced by the oxidation of all three constituents but the larger portion comes from the degradation of the cellulose and the next larger portion comes from the hemicellulose.

(2) The formic acid results mostly from the oxidation of the cellulose and hemicellulose.

(3) The acetic acid comes partly from the saponification of the acetyl groups in the lignin, but most of it comes from the oxidation of all three constituents with the hemicelluloses probably playing the most important part.

Thorn (22) was of the opinion that the oxalic acid was formed almost entirely from the carbohydrates. Lignin does give oxalic acid, but under the usual conditions of fusion none is obtained.

Potassium hydroxide gives much higher yields of the aliphatic acids than does sodium hydroxide but the increased yields do not compensate for the much greater cost. For this

reason the commercial process for the production of these acids by the fusion process is limited to the use of sodium hydroxide or sodium hydroxide mixed with smaller amounts of potassium hydroxide.

VI - EXPERIMENTAL WORK

A. Fusion With Sodium Hydroxide

The corn stalks used in the experiments were taken from one bale of a large number of bales (100 tons) of stalks which were gathered and stacked by the Agricultural Engineering Department, Iowa State College, for the Engineering Experiment Station during the winter of 1927-28. The stalks were broken up by hand and were then ground to pass a 40 mesh screen in a Wiley sample grinder.

The corn cobs used were secured from the Ames Grain and Coal Company elevator. They were of the red variety of field corn. These also were reduced to pass a 40 mesh screen by means of the Wiley sample grinder.

The oat hulls used were secured from the Quaker Oats Company at Cedar Rapids, Iowa. Since they were well divided and of fairly uniform size no further reduction was deemed necessary and they were used as received.

The sodium hydroxide used was a good grade (95 per cent) of technical flake caustic. When it was used in solution, the solution was allowed to stand until a clear supernatant layer could be decanted off. In some of the experiments the dry flake caustic was used in order to compare the results with those obtained when strong solutions were used.

The fusions were carried out in a 250 c.c. nickel crucible heated by either an air or an oil bath. In the first

runs an air bath was used but later an oil bath was used and it was found to be much more satisfactory as a more uniform temperature could be maintained. The crucible was covered with a sheet iron lid so as to exclude as much air as possible. A thermometer was hung from a support so as to extend through a hole in the center of the lid until it dipped into the charge. Stirring of the batch was accomplished with a nickel rod thrust through a slot in the lid. Another thermometer hung in the air or oil bath so that the desired heating temperature could be maintained.

The procedure was as follows: The material and the sodium hydroxide, either flake or in solution, were well mixed in the crucible and then the heating was begun. The ground stalks were very bulky and 10 grams nearly filled the crucible. The ground cobs and the oat hulls were fairly compact and filled about one-half as much space as the stalks. The oat hulls were denser than the cobs.

The following facts were noted during the course of the experiments. Most of the water comes off at about 130° C. as the temperature stays constant thereabouts for quite awhile. After most of the water has been driven off the temperature rises gradually from 130° C. to 170° C. Under the conditions which existed in these experiments this gradual rise took from one and one-half to two hours, although, of course, this period would probably vary greatly with the size of the apparatus employed and the severity of heating. At 170° C. the batch is a

yellowish brown mass and is rather pasty. Fusion sets in between 190° C. and 200° C. and at about 215° C. the mass is quite thick and viscous but it is of about the same color. The fusion is accelerated near 220° C. and at 250° C. the batch becomes thin and fluid. A marked exothermic reaction sets in between 215° - 220° C., there is evolution of gas (mostly hydrogen), and the temperature rises rapidly to 240° C or higher. At 250° C. the mixture is a lemon yellow color. The mass sets hard on cooling below 250° C. but melts again when heated to 240° C.

The fused mass after cooling was always taken up by adding water and heating until solution took place. The residues from experiments where the temperature was carried above 220° C. were extremely slight after the fused masses were treated with water. Some undissolved particles remained when the temperature was halted at 190° C. In all cases the water solutions of the residues were almost black and contained some colloidal matter. The color of the solutions was probably due to these colloidal slimes for when the solutions were filtered they were of a deep brownish red color.

The addition of acetic acid threw down some flocculent precipitate (probably a degraded cellulose) in the experiments halted at 190° C, but no precipitate came down in the experiments carried to 220° - 250° C. This would indicate that in these latter tests there was probably a complete break-down of the cellulose and incrusting substances.

In the experimental work only four variables were

changed. These were as follows: Either flake sodium hydroxide or sodium hydroxide solution was used; the ratio of weight of caustic to cellulosic material was varied, the length of time of heating and the temperature at which this heating was carried out were varied. The first factor is not important since most of the water of solution is driven off near 150° C. which temperature is far below the fusion temperature. The next factor is important both from an economical and a technical standpoint. It is desirable to use as small an amount of caustic as possible but when too small a ratio is used the batch chars easily and is rendered worthless. Other investigators, (24) working on various woods have found a ratio of three parts of caustic to one of material to be satisfactory and this ratio was also found to be satisfactory for the materials being investigated. However ratios of one, two and four were also used.

It was the purpose of the investigation to determine the optimum conditions for securing high yields of both oxalic and acetic acids simultaneously, or if this was found to be impossible, to determine what factors influenced the production of high yields of either acid.

The materials used, time and temperature of the heating periods, and the results of the first series of experiments are given in the following table.

Material	Temp. :°C.	Heating :Time	Sp. Gr. :of	Ratio :NaOH to	Total :Vola-	Acetic :Acid	Oxalic :Acid
		:at Max. :Temp.	:NaOH :Sol.	:material :(Air	:tile :Acid	:Per :Cent	:Per :Cent
			: (Approx. :40%)	: dry)	: Calc.as: :Acetic :Acid		
					: %		
Corn cobs	: 190	: 1 hour	: 1.44	: 5:1	: 15.42	: 6.87	: 8.34
" "	: 220	: "	: "	: "	: 23.60	: 18.41	: 25.44
" "	: 250	: "	: "	: "	: 20.49	: 10.89	: -
Corn stalks	: 190	: "	: "	: "	: 16.60	: 8.55	: 10.36
" "	: 220	: "	: "	: "	: 23.45	: 18.93	: 35.56
" "	: 250	: "	: "	: "	: 21.13	: 15.95	: 7.71
Oat hulls	: 190	: "	: "	: "	: 16.20	: 10.30	: 25.00
" "	: 220	: "	: "	: "	: 23.98	: 12.45	: 26.00
" "	: 250	: "	: "	: "	: 19.45	: 18.00	: 16.44

In all the above experiments the preliminary heating was so gradual that a period of about three hours was required to bring the batch up to the maximum temperature.

Another series of fifteen experiments was carried out with the cooperation of Mr. J. B. Williams. In this series the sodium hydroxide (technical flake caustic) was used in the dry state and both the ratio of caustic to material and the heating periods were varied. Details of each experiment are given and these are followed by a summarized table of results.

Experiment -1.

Ratio of caustic to cobs was 1:1. The batch was heated until the exothermic reaction took place (about 210° C.) and the temperature rose to 240° C. Heat was then applied to keep the temperature at 240° C. but soon the temperature rose to about 290° C. and the mass charred. The charred residue was not

analyzed as it appeared to be entirely carbonaceous material.

Experiment #2.

Ratio of caustic to cobs was 2:1. The batch was heated until the temperature reached 190° C. Heating was then discontinued but the temperature rose until the exothermic reaction set in and a temperature of 230° C. was reached. The residue was dark yellow in color and there was a considerable amount that had not been disintegrated.

Oxalic Acid 16.59 per cent.

Acetic Acid 6.77 " "

Experiment #3.

Ratio of caustic to cobs was 2:1. The batch was heated to 200° C. Heating was discontinued and the exothermic reaction took place. The temperature rose to 241° C. The batch was not heated further. There was considerable residue left after treating the mass with water.

Oxalic Acid 14.68 per cent.

Acetic Acid 9.68 " "

Experiment #4.

Ratio of caustic to cobs was 2:1. The batch was heated to 200° C. Heating was discontinued while the exothermic reaction took place. The temperature reached 240° C. and heat was applied to maintain the temperature at 240° C. The temperature rose suddenly and the batch charred. The mass was not analyzed.

Experiment #5.

This test was a repetition of Experiment #4 but the same unsuccessful results were obtained due to the batch charring.

Experiment #6.

Ratio of caustic to cobs was 2.5:1. The batch was heated to 200° C. and then the heating was discontinued. The exothermic reaction set in and the temperature rose to 220° C. No further heating was done. The fused mass was dark yellow in color and contained a small amount of water insoluble residue.

Oxalic Acid 12.87 per cent.

Acetic Acid 13.72 " "

Experiment #7.

Ratio of caustic to cobs was 2.5:1. The batch was heated until the temperature reached 210° C. The source of heat supply was then removed while the exothermic reaction took place. The highest temperature during this reaction was 228° C. No further heating was done. The product was dark yellow in color and a small amount of water insoluble residue remained after the mass was taken up with water.

Oxalic Acid 12.62 per cent.

Acetic Acid 12.00 " "

Experiment #8.

Ratio of caustic to cobs was 2.5:1. The source of

heat was removed when the batch temperature reached 215° C. The highest temperature reached during the exothermic reaction was 238° C. The mass was not heated further. The product was light brown in color and contained a small amount of water insoluble material.

Oxalic Acid 16.29 per cent.

Acetic Acid 15.10 " "

Experiment #9.

Ratio of caustic to cobs was 2.5:1. The initial part of this run was a duplicate of Experiment #8. The highest exothermic temperature reached was 242° C. After the exothermic reaction had subsided heat was applied and the batch was kept at a temperature of 235° C. for ten minutes. Then the temperature rose suddenly and the mass charred. The charred product was not analyzed.

Experiment #10.

Ratio of caustic to cobs was 3:1. The batch was heated in an oil bath. The temperature of the oil bath was brought to 215° C. and held there until the exothermic reaction took place. The batch temperature at which the exothermic reaction started was about 218° C. The fused mass set hard or "froze" after the reaction subsided. The highest temperature during the reaction was 242° C. No further heating was done. The product was light yellow in color and contained very little water insoluble material.

Oxalic Acid 50.33 per cent.
 Acetic Acid 20.22 " "

Experiment #11.

Ratio of caustic to cobs was 3:1. The temperature of the oil bath was brought to 240° C. The exothermic reaction started when the batch temperature reached 215° C. and the highest temperature reached was 228° C. The fusion was then heated for one hour at 240° C. The product was yellowish brown in color and contained very little water insoluble material.

Oxalic Acid 26.09 per cent.
 Acetic Acid 20.42 " "

Experiment #12.

The ratio of caustic to cobs was 3:1. This run was a duplicate of Experiment #11 except the fusion was heated for two hours at a temperature of 245° C. after the exothermic reaction had subsided. The fusion was dark yellow and the color darkened as the heating was continued, due no doubt to oxidation. There was practically no water insoluble material.

Oxalic Acid 36.10 per cent
 Acetic Acid 21.09 " "

Experiment #13.

Ratio of caustic to cobs was 3:1. The oil bath temperature was quickly brought to 245° C. and held constant. The

exothermic reaction started at a batch temperature of 218°C . The maximum temperature reached was 251°C . At this point the fused mass was light yellow in color. The fusion was then kept for two hours at $255-258^{\circ}\text{C}$. The color changed gradually to a dark brown. Heating at an oil bath temperature of 245°C . was still continued for another one and three-quarter hours but the batch temperature gradually dropped. The color changed to a very pale yellow. The fusion stood over night before being taken up in water.

Oxalic Acid 14.22 per cent

Acetic Acid 20.70 " "

Experiment #14.

Ratio of caustic to cobs was 5:1. This run was as near as possible a duplicate of Experiment #13.

Oxalic Acid 17.10 per cent.

Acetic Acid 17.90 " "

Experiment #15.

Ratio of caustic to cobs was 5:1. This run was an endeavor to duplicate #12.

Oxalic Acid 31.10 per cent

Acetic Acid 21.65 " "

The results of this series of experiments are shown in the following table. In this table there is also included a column giving the formic acid yield for each run. The oxalic acid yields in all cases are given as crystallized oxalic acid

($3\text{H}_2\text{O} \cdot 2\text{H}_2\text{O}$). The weight of the ground cobs is on the air dry basis. The solid sodium hydroxide used was the technical grade caustic (76 per cent Na_2O content).

Run: Weight in Grams: Ratio :				Yield			
No.:	Cobs :	NaOH :	NaOH : Cobs	Total Volu- :tile Acid	Acetic :Acid	Formic :Acid	Oxalic :Acid
:	:	:	:	:Calc. to	:Per	:Per	:Per cent
:	:	:	:	:Per cent	:cent	:cent	:(air dry
:	:	:	:	:Acetic (air:	:	:	:basis)
:	:	:	:	:dry basis)	:	:	:
1 :	10 :	10 :	1:1*	-	-	-	-
2 :	" :	20 :	2:1	25.74	6.77	12.64	16.59
3 :	" :	" :	2:1	26.06	9.68	12.26	14.68
4 :	" :	" :	2:1*	-	-	-	-
5 :	" :	" :	2:1*	-	-	-	-
6 :	" :	25 :	2.5:1	22.73	13.72	6.06	12.87
7 :	" :	" :	2.5:1	26.41	12.00	9.60	12.62
8 :	" :	" :	2.5:1	30.40	15.10	10.20	16.29
9 :	" :	" :	2.5:1*	-	-	-	-
10 :	" :	30 :	3:1	25.05	20.22	1.87	50.35
11 :	" :	" :	3:1	25.22	20.42	1.87	26.09
12 :	" :	" :	3:1	24.77	21.09	2.45	36.10
13 :	" :	" :	3:1	20.90	20.70	0.126	14.22
14 :	" :	" :	3:1	18.32	17.90	0.26	17.10
15 :	" :	" :	3:1	25.16	21.66	2.33	31.10

*Charred.

In cooperation with Mr. K. M. Vaughn some experiments with caustic fusions using corn cobs and sodium hydroxide were made. The primary purpose of these experiments was to secure a resultant mixture of sodium hydroxide and sodium oxalate that could be used satisfactorily as a water softening mixture. The action of these two reagents in combination as a water softening mixture will not be taken up in this paper but the reader is referred to Mr. Vaughn's thesis (25). The yields of sodium oxalate

secured in the various runs will be given however as this part of the work falls within the scope of this thesis.

When caustic fusions are made in which the ratio of sodium hydroxide to corn cobs is 3:1 or greater a residue can be secured under proper conditions which will soften water satisfactorily but it has the drawback of making the treated water too caustic due to the excess of sodium hydroxide in the product. A ratio of six parts of sodium oxalate to one part of sodium hydroxide is the theoretical correct proportion for Ames water and therefore in these experiments a smaller ratio than 3:1 was used so as to secure a product which contained a smaller amount of excess caustic. The results of the runs are given in the following table.

No.:	Grams NaOH	Grams Cobs	Sodium Oxalate: in Grams	Excess NaOH: in Grams
1 :	100	40	4.90	70.7
2 :	80	40	3.32	50.5
3 :	90	40	9.40	60.5
4* :	35	40	-	-
5* :	40	40	-	-
6* :	40	40	-	-
7' :	40	40	-	-
8' :	40	40	-	-
9* :	40	40	-	-
10 :	100	100	8.67	29.2
11 :	100	100	10.70	28.8
12 :	50	50	33.28	11.0
13 :	100	100	20.80	25.0

*Batch charred.

'No fusion.

On the whole the results were not very satisfactory. When using such a small ratio of caustic to cobs it is very difficult to secure a fusion without charring the batch. In the best run, #12, a ratio of sodium oxalate to caustic of 3 to 1 was obtained. This was the nearest approach to the theoretical desired ratio of 6:1 for Ames water.

In cooperation with Mr. J. B. Williams and Mr. R. Roberts some fusions were made using flake sodium hydroxide and corn cobs. A ratio of 3 parts of caustic to 1 part of cobs was used. The batches were heated to the fusion temperature of 220° C. and after the exothermic reaction had taken place the fused masses were allowed to cool and were then taken up in water. The primary object of these experiments was to secure fusion products for the continuation of studies similar to those of Vaughn (25) on the water softening properties of the residues containing sodium hydroxide, sodium oxalate and sodium carbonate.

After the fused residues were dissolved in water the resultant solutions were analyzed for oxalic acid, sodium hydroxide and sodium carbonate. The oxalic acid was determined in the manner given in methods of analysis. Total alkalinity was determined by titration with standard hydrochloric acid and methyl orange. Causticity was determined by precipitating the carbonate with excess barium chloride in boiling solution, filtering off the precipitate and titrating the filtrate with standard hydrochloric acid using methyl orange as indicator. The results checked those using differential titration, using first phenol-

phthalein and then methyl orange. The results are given in the following table. (Ten grams of cobs and thirty grams of sodium hydroxide were used in each case.)

Experiment	:NaOH in Residue: : Grams	:Na ₂ CO ₃ in Re- :sidue : Grams	:Oxalic Acid Per :cent Based on :Weight of cobs :Used
1	15.5	1.50	17.00
2	13.0	3.65	15.24
3	17.6	4.13	12.98
4	17.0	2.25	17.80
5	16.5	3.00	18.50
6	19.8	3.00	30.50
7	23.2	6.75	33.00
8	18.6	5.78	30.40

A study of the results obtained in the experimental work brings out the following facts. The ground corn stalks are much bulkier than ground corn cobs or oat hulls and a commercial reaction vessel in which ground stalks were to be fused would have to be approximately twice as large as one which would hold an equal weight of ground cobs. The same ratio would hold if the whole cobs were used and the stalks were broken to about the size of the whole cobs. Oat hulls occupy about two-thirds the space taken up by an equal weight of ground cobs.

A ratio of one part of caustic to one part of stalks or cobs is entirely unsatisfactory as the batch is hard to stir and charring takes place very easily. A ratio of two to one is somewhat better but the fusion requires very close attention and constant stirring to prevent charring. The yields of desir-

able products are lower than when larger ratios are used, and the decomposition of the carbohydrate material is not complete due to incomplete fusion. Using a two to one ratio the fusion can be carried through the exothermic reaction if the stirring is vigorous but if heating is continued after the exothermic reaction has taken place charring almost invariably takes place within a few moments.

When a ratio of two and one-half parts to one is used still better results are secured but the success of the run depends upon complete and vigorous stirring which tends to prevent charring and the yields of desirable products are lower than when a higher ratio is used.

A ratio of three parts of sodium hydroxide to one part of stalks or cobs seems to be entirely satisfactory. This ratio gives a fusion which is so fluid that it is easy to work and after the exothermic reaction has taken place heating at a high temperature can be continued if desired without charring taking place. Satisfactory yields of desirable products can be secured under the proper conditions and it would appear that the ratio 3:1 is probably the economic limit.

The results show that for one hour heating periods at 190°C , 220°C , and 250°C , corn stalks and cobs give almost identical yields of acetic acid at the respective temperatures. The yield of acetic acid is greatest when the temperature is held at 220°C . Oat hulls give a slightly less yield than stalks or

cobs at 220°C but a somewhat higher yield at 250°C . The yield of acetic acid from cobs is increased slightly by heating for two hours instead of one hour.

It is quite evident that a temperature of 190°C (somewhat below the fusion temperature) favors the formation of formic acid and again at high temperatures (250°C and above) formic acid seems to be formed at the expense of oxalic acid. There seems to be no correlation between the yield of acetic and oxalic acids, but there is a correlation between the yields of formic and oxalic acids. At 190°C or thereabouts formic acid is formed in quantity but the yield of oxalic acid is low. Around 220°C the yield of oxalic acid is increased at the expense of formic acid but at higher temperatures the reverse is true and the oxalic acid seems to break down, at least in part, to formic acid.

A temperature of from 220°C - 245°C therefore seems to be the optimum range for the formation of both acetic and oxalic acid from corn cobs and stalks. A heating period of one hour in this range gives a good yield of both products but these yields can be increased slightly by heating for two hours. It is doubtful if the slight increase in yields would compensate for the extra fuel needed to prolong the heating period beyond one hour. Oat hulls give a higher yield of oxalic acid at 190°C than do corn stalks or cobs but at the higher temperatures the yields are of about the same order. When the fused masses of stalks and cobs are heated for more than two hours at about 240°C

the product begins to darken and char and the yield of oxalic acid is lessened.

The following tables show the yields obtained from stalks, cobs, oat hulls and elm sawdust under approximately the same conditions. The results are in per cents of air dry material.

190° C.						
Material	Hours	Total	Volatile	Acetic	Formic	Oxalic
	Time		Acids	Acid	Acid	Acid
Oat Hulls	1	16.25	10.30	8.53	25.00	
Corn Stalks	1	16.60	8.55	8.05	10.36	
Corn Cobs	1	15.42	6.87	8.55	8.34	
Elm (200°C)	3/4	16.10	9.00	-	-	
Elm (200°C)	1 1/2	17.30	9.00	-	24.30	

220° C.						
Material	Hours	Total	Volatile	Acetic	Formic	Oxalic
	Time		Acids	Acid	Acid	Acid
Oat Hulls	1	23.98	12.45	11.55	23.00	
Corn Stalks	1	23.45	18.93	4.52	35.56	
Corn Cobs	1	23.60	18.41	5.19	25.44	
230° C.						
Elm	3/4	21.25	11.65	-	-	
Elm	1 1/2	22.25	14.10	-	30.80	

250° C.						
Material	Hours	Total	Volatile	Acetic	Formic	Oxalic
	Time		Acids	Acid	Acid	Acid
Oat Hulls	1	19.45	18.00	1.45	16.44	
Corn Stalks	1	21.13	15.95	5.18	7.71	
Corn Cobs	1	20.49	10.89	9.60	-	
260° C.						
Elm	3/4	16.20	16.50	-	-	
Elm	1 1/2	18.00	15.00	-	-	

A comparison of these results shows that at temperatures below the fusing point (190° - 220° C) the yield of oxalic acid is less from stalks and cobs than from elm sawdust but that the yield of total volatile acids and of acetic acid is about the same. At 220° - 230° C. the yield of oxalic acid is about the same from all, but the yield of acetic acid from stalks and cobs reaches a maximum within this range while for oat hulls and elm sawdust the optimum range is 250° - 260° C. Oat hulls appear to act quite similar to elm sawdust in this reaction.

B. Recovery of the Sodium Hydroxide

In the fusion process, as well as in the nitric acid oxidation process, a large part of the reagent used must be recovered in order to make the process commercially feasible. As determined experimentally a large excess of the alkali must be used in order to prevent charring of the organic material, to give good yields of acetic and oxalic acids and to give a workable fused mass.

As regards the sodium hydroxide used, some goes through the fusion process unchanged, some is converted to sodium carbonate and some forms the sodium salts of the acetic, formic and oxalic acids.

Mahood and Cable (24) in studying the recovery of the alkali from fusions of various wood sawdusts used the following procedure.

The melt was dissolved in water and then gassed with carbon dioxide until all the sodium hydroxide present was converted to sodium carbonate, that is until the solution no longer reacted alkaline to phenolphthalein after treatment with excess of barium chloride. The solution was then concentrated and allowed to crystallize at room temperature so as to bring about the formation of sal soda, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The crystallization was hastened by seeding. The sodium carbonate crystals were then filtered off and washed three times. By this method 96 to 99 per cent of the acetic acid was recovered but 45 to 48 per

cent of the alkali remained in the mother liquor and wash waters so another procedure was tried. It was as follows.

(1) First washings from previous runs were added to the original solution; the solution was then treated with carbon dioxide, concentrated, and the carbonate "seeded" out.

(2) Second washings from previous runs were used for first washing.

(3) Third washings from previous runs were used for the second washing.

(4) Fresh water was used for the third washing.

This procedure resulted in a 95.9 per cent recovery of the acetic acid and 20.1 per cent of the alkali was left in the mother liquor. By employing refrigeration during the crystallization process, the crystallizing temperature was reduced to 0° C. and at this low temperature only 9 per cent of the alkali was left in the mother liquor and of this amount 60 per cent or 5.4 per cent of the total alkali was combined with the acetic acid as sodium acetate. The crystals of sodium carbonate obtained were sufficiently free from organic matter to make calcining unnecessary before causticizing the soda ash to hydroxide with lime. It was estimated that an 85 to 90 per cent alkali recovery could be obtained commercially in this manner.

The greater portion of the acetic acid (96 per cent), which is present as its sodium salt, remains in the mother liquor as sodium acetate is very soluble in cold water. The acetic

acid can be recovered by adding sulphuric acid in excess to the residual mother liquor and distilling off the volatile acetic acid. This crude acetic acid can then be fractionated to give the strength found on the market, which is about 30 per cent acetic acid.

In the fusion process formerly employed in Europe, in which sawdust was fused with sodium hydroxide or a mixture of sodium and potassium hydroxides, the oxalic acid only was recovered. Dale (20) in carrying out his commercial process in England used the following procedure.

The fused mass, while still hot, was dissolved in water and the solution filtered and concentrated to 38° Be. When cold, the solution deposited crude sodium oxalate, which was filtered off and dissolved in a small quantity of boiling water. Lime was next added to the hot solution to precipitate the oxalic acid as insoluble calcium oxalate. The precipitate was made into a paste with water and the oxalic acid liberated by addition of sulphuric acid. The liquid was decanted and concentrated until all the calcium sulphate separated out. Then the oxalic acid was allowed to crystallize out and was purified by repeated recrystallization.

If the fusion process is used to produce both acetic and oxalic acid the following method of operation can be used. The fusion is leached with water and gassed with carbon dioxide until excess hydroxide is converted to carbonate. The solution

is concentrated and crystallized at a low temperature using refrigeration. The sodium carbonate and oxalate crystallize out and are washed by counter current washing so as to secure a high yield of sodium acetate and a high percentage recovery of the alkali.

The sodium acetate in the mother liquor can be converted to acetic acid with sulphuric acid. The acetic acid is then boiled off and concentrated by distillation.

The sodium oxalate can be separated from the sodium carbonate by solution and fractional crystallization, or it can be separated as insoluble calcium oxalate by adding just enough lime to the solution to precipitate the oxalate and not the carbonate. After separation by filtering, the calcium oxalate is then decomposed with sulphuric acid and the resulting oxalic acid purified by recrystallization.

The sodium carbonate is causticized with lime. This produces sodium hydroxide which goes into a new fusion mixture while the calcium carbonate formed as a by-product is reburned to lime or it can be wasted. If the calcium carbonate is reburned to lime, the carbon dioxide given off can be used to gas the solution of the fused mass. In case raw limestone is burned to produce the lime necessary for causticizing the carbon dioxide formed can be used for gassing. Since both lime and carbon dioxide are necessary for this method of recovery it would seem to be more economical to have a lime kiln as part of

the necessary plant rather than to buy lime and use cylinders of carbon dioxide.

C. Methods of Analysis

The product resulting from the fusion of the organic material, corn stalks or cobs or oat hulls with sodium hydroxide was dissolved in distilled water and the solution made up to 500 cc. For the determination of the total volatile acids, 100 c.c. of the solution were taken, 15 c.c. of 85 per cent (syrupy) phosphoric acid were added and the mixture was distilled until approximately 50 c.c. remained in the distilling flask. 50 c.c. more of distilled water were added to the distilling flask through a dropping funnel and the distillation was continued. The additions of 50 c.c. portions of distilled water were continued in this manner until 400 c.c. of distillate were collected. This distillate was made up to 500 c.c. with distilled water. 100 c.c. of this solution were taken and titrated with 0.1N sodium hydroxide. Phenolphthalein was used as the indicator. This titration gave the total volatile acids, i. e. acetic and formic. The results were calculated to per cent acetic acid.

To determine the formic acid content, 100 c.c. of the distillate were taken and treated with grams of mercuric oxide equal to the number of c.c. of 0.1N sodium hydroxide used in the titration for total volatile acids. This was digested for three hours on a boiling water bath to destroy the formic acid and at the end of the three hours 25 c.c. of 85 per cent phosphoric acid were added and the contents distilled. The distilla-

tion was continued in the same manner as before until 250 c.c. were collected. This distillate contained only acetic acid and was titrated with 0.1N sodium hydroxide using phenolphthalein as an indicator. Results were calculated to per cent acetic acid. The difference between the per cent acetic acid calculated for total volatile acids and the per cent acetic acid calculated from the results of the second titration gave the per cent of formic acid calculated to acetic acid. This value times the ratio of the molecular weight of formic acid to that of acetic acid gave the per cent of formic acid which is shown in the tables of results.

The oxalic acid was determined by taking 25 c.c. of the solution, acidifying this with acetic acid and boiling until the carbon dioxide was driven off. The hot solution was then made alkaline with ammonium hydroxide and any iron which precipitated was filtered off. The precipitate was washed with hot water. The filtrate was heated to boiling and a saturated solution of calcium acetate was added in excess (about 50 c.c.). The precipitate of calcium oxalate was allowed to settle. Then it was filtered on an ashless filter paper and allowed to dry. When dry, the filter paper was burned off and the precipitate of calcium oxalate was ignited at a red heat for about an hour. The residue when cool was moistened with a few drops of concentrated sulphuric acid, then the sulphur trioxide fumes were driven off, using a hot air bath to prevent spatter-

ing, and the residue was heated for one hour at a dull red heat. The oxalic acid in the sample was calculated to

$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ from the weight of the calcium sulphate.

VII - SUMMARY

FUSION WITH SODIUM HYDROXIDE

The results of the experimental work done on the fusion of corn cobs and stalks with sodium hydroxide to produce acetic, oxalic, and formic acids can be summarized as follows:

(1) The ratio by weight of alkali to cobs or stalks should be at least 3:1 in order to prevent charring, give good yields of the desired products, and give a workable fusion mixture.

(2) Cobs and stalks give almost identical yields of the reaction products under the same conditions but ground cobs occupy much less space (about one-half) for a given weight and seem to be easier to work.

(3) The optimum conditions for the production of both oxalic and acetic acids are a heating period of from one to two hours at a temperature of from 220°C to 250°C.

Under the above conditions the yield of acetic acid is about 20 per cent of the weight of the air dry cobs or stalks, and the yield of oxalic acid is about 30 to 55 per cent of the weight of the air dry material.

(4) The yield of acetic acid seems to bear no relation to the yield of oxalic acid.

(5) There seems to be a close relation between the yields of formic and oxalic acids. At temperatures below the

optimum (around 190°C - 200°C) the yield of formic acid is relatively high while the yield of oxalic acid is low.

Within the optimum temperature range the yield of oxalic acid increases at the expense of the formic acid. At higher temperatures the yield of oxalic acid decreases while the yield of formic acid increases somewhat.

(6) It is immaterial whether the alkali be added to the cobs and stalks in the dry state or in solution as most of the water is boiled off at a relatively low temperature.

(7) Under similar conditions the yields of the reaction products from cobs and stalks are fairly close to the yields obtained from elm sawdust.

(8) The optimum conditions for cobs and stalks are less drastic than those required for wood sawdusts; the temperature being somewhat lower, and the heating period somewhat shorter.

(9) Cobs and stalks give yields of acetic acid comparable to those obtained from wood sawdusts, but the yields of oxalic acid are somewhat lower, being especially lower than those obtained from soft woods like pine. In this process cobs and stalks seem to resemble the hard woods more than they do the soft woods.

(10) The residue left from a good fusion is very small in amount and seems to consist of degraded cellulose in an almost colloidal state of subdivision. It is probably

worthless as a cellulose material both because of its fineness and because the conditions under which it is produced are so drastic that it has lost its characteristic resistance to the action of chemical reagents.

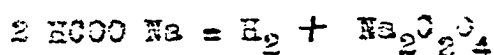
The fusion process, using cobs or stalks and sodium hydroxide, seems to be commercially feasible. Cobs or stalks can be successfully substituted for wood sawdusts especially if acetic acid is the main product desired. The cubical capacity of the fusion apparatus would be about the same for a given weight of ground cobs or sawdust but would have to be somewhat greater for the same amount of stalks.

At the present time when acetic acid is in such great demand the fusion process can probably be successfully revived. The oxalic acid in this case would be handled as a by-product. The writer has been informed recently by a representative of one of the largest producers of solvents in the United States that his concern, through research suggested by the previous work in the Chemical Engineering Department, Iowa State College, has had such success that they are starting a semicommercial scale plant to give the process a test on a large scale.

They found that the reaction was very delicate being quite susceptible to temperature changes, but they believe that they have determined the optimum conditions for the production of acetic acid. The conditions were not revealed but it was stated that the acetic acid yield was around 20 per cent, and it is believed that they are using corn cobs as the raw material.

The dilute acetic acid made by this process is to be used by the company in their own products and is not to be marketed. The oxalic acid will probably be put on the market as a valuable by-product. It was estimated by them that if the process was successful in producing the desired amount of acetic acid, the amount of oxalic acid produced as a by-product would be sufficient to supply the entire domestic consumption at the present time.

One of the products that made this process attractive to the company was the hydrogen evolved during the fusion. Probably most of the hydrogen results from the decomposition of the sodium formate to oxalate as shown by the equation



It has been found that about 12 per cent of formic acid is formed in the early stages of the process but only about 2 per cent is present in the finished product. (These per cents are calculated as formic acid and not as sodium formate). An approximation of the amount of hydrogen formed can be calculated as follows:

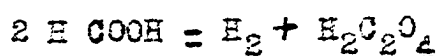
Basis 100 lbs. air dry cobs.

12 per cent of 100 lbs. = 12 lbs.

2 " " " " " = 2 "

Pounds of formic acid

decomposed = 10 lbs.



$$2(46) : 2 = 10:x$$

$$x = 0.217 \text{ lbs. H}_2/100\% \text{ coals.}$$

$$0.217\% \text{ H}_2 = 39 \text{ cu. ft. H}_2 \text{ at S. G.}$$

They plan to use the hydrogen evolved in the production of synthetic methanol or ammonia.

PART II

STUDIES ON CORN STALK CELLULOSE

I - INTRODUCTION

Cellulose at the present time serves as a raw material for so many important industries that this era is sometimes called the "Cellulose Age". If this is the status at present, it will probably be even more pronounced in the future as the structure of the cellulose molecule is gradually worked out thus bringing about the development of many new and important cellulose products.

The position of cellulose in the field of the organic industries is often likened to the position that iron occupies in the metallurgical field. There is an interesting comparison between these two materials. Each in its field can not be replaced by any other material. Both occur widely distributed but usually in combination with other substances, and they must be purified before being used. Iron is important because of its desirable mechanical properties but it is one of the most susceptible of all the metals to corrosion, especially that induced by air and water. On the other hand cellulose, while its mechanical properties are not pronounced, is one of the most inert of all organic substances, and its power of resistance to the action of chemical reagents is perhaps the most important property that gives it its present distinction.

At the present time the demands of the industries for cellulose are becoming so great that the present sources give

indication of being rapidly depleted. Cotton, a natural cellulose which occurs in the purest form of all cellulose, long ago became too expensive to use in many of the cellulose industries, and also its properties restricted its use to important but special applications.

Other forms of cellulose have been introduced to supply the general demand, and of these forms, the lignocelluloses, represented by the various woods, are at present the most important. To supply the tremendous consumption of the present day the desirable woods have been cut at a terrific rate and the future promises an even greater consumption. In spite of extensive reforestation the pulp mills are gradually pushing further and further into the remaining forests, and the prices of pulp over an interval of years show quite a rapid and consistent increase. Although the forest lands represent perhaps the greatest concentration of cellulose per acre, the time required to reproduce the yield when once the land has been cleared is so great that consumption is drawing far ahead of any possible yields from reforestation.

These factors have created a condition which at the present time is drawing the attention of the cellulose industries to other possible sources. This attention recently has become centered on the cereal straws as potential sources for the future. Among these materials probably the most important are the wheat, oat, and rice straws, bamboo and other canes, and corn stalks. These materials have not in the past been

favorably received by the cellulose industries for a variety of reasons, the most important one being probably that wood was first utilized because of its apparently greater concentration. The technique of pulp extraction from wood therefore grew up under the influence of the characteristic properties of the woods, and the properties of the pulps secured therefrom defined the specifications that the cellulose industries considered essential for satisfactory products. These conditions have created a prejudice against the perennial plants that is quite strong even today, but there are plentiful indications at present that in many places this prejudice is being broken down, and the cellulose industries are beginning to realize that the technique of pulp extraction from the woods is perhaps not the most suitable for pulp extraction from the straws and canes; also, that perhaps different specifications should be drawn for cellulose obtained from these annual sources when used for many materials for which they are perfectly satisfactory, but in the production of which they are handicapped by unfair specifications.

The utilization of plants which have a short life cycle, especially annual plants which are largely waste agricultural by-products, therefore offers a real solution to the problem of ever increasing consumption of cellulose products. Furthermore, the use of such materials would transfer the cellulose industries from isolated regions in the north to centers of population, where the distance from production to consumption

would not be so great as at present.

Among the agricultural wastes that are possible sources of cellulose probably the most interesting one to the people of the United States, and especially of the Middle West, is the corn stalk. The tremendous yearly production of this plant is one of the factors that will influence its future use. It is estimated that between 150-175 million tons of corn stalks are produced each year in the United States. The larger portion of this production is concentrated in a relatively few states of the Middle West known as the Corn Belt. In this area an average of two tons of stalks to the acre can be expected under normal conditions. This concentration of pulp material compares favorably with that of forest lands, and has the immense advantage of yearly renewal. Furthermore, the Corn Belt is close to the center of population in the United States, and the distance from producer to consumer would be materially shortened if the cellulose industries could be located in the Corn Belt region.

To initiate any raw material into the industries requires thorough studies of its properties. Woods, in spite of the fact that they have been used for years in the cellulose industries, are constantly being studied so that the methods of pulp extraction and the quality of cellulose products can be improved. Therefore, if corn stalks are to be used in an extensive way as a source of cellulose it will be necessary to make a very thorough study of the stalk in regard to its chemi-

cal constitution, physical properties, effects of the known methods of pulp extraction and many other problems concerned with its utilization. It was with the hope that it would be of some value in the commercial utilization of corn stalk cellulose that the work recorded in this part was performed.

II - THEORY

THE CONSTITUENT GROUPS OF THE LIGNOCELLULOSES

The greater portion of the cellulose used in the cellulose industries occurs in nature combined with other substances, and the various pulping processes have as their object the purification of the cellulose from these incrustants. These cellulose complexes are usually classified as follows:

1. Lignocelluloses contain lignin; wood, straw, and jute are examples of this class.
2. Pectocelluloses and mucocelluloses contain pectic and mucilaginous or gummy substances; the former are represented by hemp, flax, and ramie, and the latter by algae and various fruits and tubers.
3. Adipocelluloses and cutocelluloses contain waxy and fatty compounds. Cork, an adipocellulose contains among other substances phellonic and suberic acids.

The lignocelluloses are by far the most important class to the cellulose industries, and of these only a few are used to any great extent, due to very exacting specifications. The wood pulp industry at present is practically based upon the utilization of coniferous woods and poplar.

The lignocelluloses are sometimes further divided into three groups depending upon their pentosan content. Under this grouping the cereal straws and similar materials, make up one class due to their high pentosan content, while various kinds of wood make up the other two classes with lower pentosan

contents.

There has been an immense amount of work done in the last one hundred years on the nature of the lignocelluloses and cellulose compounds in general. It is estimated that in the last fifty years there have been over 40,000 papers published on cellulose and its compounds. In spite of this great effort the chemistry of cellulose is still today an unsolved problem.

A great deal of the work in the past has been concerned with the methods of extracting cellulose from its compounds, and relatively little has been done on the structure of the cellulose molecule itself. The work that has been performed, however, showed that it would be practically impossible to solve the structure of the cellulose molecule with chemical methods alone. Therefore, at present a large part of the research is being carried on using physico-chemical methods. Many of these have been perfected only in recent years to the stage where they are useful for such studies. Probably the tool used most extensively at present is the X-ray spectra. Great advances are being made at present from the study of X-ray spectrograms of cellulose and its compounds. These spectrograms are made by the method developed by the Braggs in which the X-rays are reflected from atomic planes parallel to the smooth surface of an oriented crystal. The method of most general application consists in subjecting a narrow tube, containing the finely powdered substance to be examined, to a rib-

bon-like beam of X-rays. With a finely powdered crystalline substance, the atomic planes are oriented in all directions, but only those planes that chance to lie in the proper direction are effective. The diffracted rays are registered on a film as a series of parallel lines of varying intensity and characteristic pattern. The X-ray examination of cellulose indicates that it is crystalline. Cotton, ramie, and wood pulp that had been reduced to a fine state of division by exposure to the vapors of hydrochloric acid gave identical patterns; hence their crystalline forms were identical.

The lignocelluloses are composed of the major constituents, cellulose, lignin, and hemicelluloses, and some minor constituents such as ash, protein, tannins, fats and resins.

Since cellulose is the most important constituent it will be briefly discussed first. The empirical formula for cellulose is $(C_6H_{10}O_5)$ usually taken n times, and it belongs to that great group of organic compounds called the carbohydrates. The number of cellulose units in the molecule is not known for sure at present but recent studies using X-ray spectrograms seem to indicate that at least 1500 to 2000 $C_6H_{10}O_5$ groups are joined to give one particle. It is believed, from these studies, that the cellulose crystal or particle is composed of chains of 30 to 40 $C_6H_{10}O_5$ groups which are arranged in parallel bundles and held together in lots of 40 to 60 chains by micellar forces. The bundles can be split up by reagents to bring about certain characteristic reactions of cellulose, but if the main chains

are broken up by the reagents a whole range of decomposition products are obtained depending upon the treatment, and swelling and dissolution of the cellulose are apt to occur.

Cellulose can be hydrolyzed to glucose in practically quantitative yield, showing that it may consist entirely of anhydroglucose units. Each cellulose unit contains three free hydroxyl groups, one of which is primary, the remainder secondary. Their position is established by the formation of 2, 3, 6-trimethylglucose. Acetolysis of cellulose gives from 55 to 60 per cent of cellobiose, an isomer of maltose, indicating that the glucose units are united wholly or in large part by cellobiose linkages. When hydrolyzed under the influence of enzyme *cytase*, cellulose breaks down, first into cellobiose, and then into glucose. It has been shown by some investigators that cellobiose preexists in the cellulose molecule, and, therefore, they consider that cellulose is built up from cellobiose and not from glucose residues. Others, as stated above, believe the glucose units are held together largely by cellobiose linkages. Although only about 60 per cent of cellobiose is obtained by acetolysis it is believed that a considerable part of the cellulose is hydrolyzed to glucose or destroyed during the treatment.

Cellulose is acted upon by caustic alkalis in a variety of ways. When fused with the alkalis, it is decomposed into oxalic, acetic, and other aliphatic acids. When treated with strong solutions (15-20 per cent) of caustic soda, cellu-

lose fibers thicken, uncurl, and become translucent, thus resembling silk fibers, if the fibers are held in tension. This process is known as mercerizing after John Mercer who first showed its commercial possibilities. It is not known for sure whether the hydroxide is combined chemically or adsorbed mechanically, but it can readily be washed out by treating the mercerized cellulose with dilute acetic acid. Very dilute solutions of caustic soda have but little effect on cellulose if the air is excluded. If the air is not excluded, some oxidation of the cellulose takes place with the formation of oxycellulose, a less resistant modification of cellulose containing less carbon and more oxygen than normal cellulose.

Cellulose is also acted upon by acids in various ways. Oxidizing acids, such as nitric and chromic convert it, at least partially, into oxycellulose if the acids are dilute or moderately strong. Very strong oxidizing acids decompose the cellulose with the production of various soluble intermediates and aliphatic acids such as oxalic. Dilute hydrolyzing acids convert cellulose to hydrocellulose, a substance having the formula $C_{12}H_{22}O_{11}$. The properties of both this substance and oxycellulose are such as to render them undesirable in the cellulose industries, and during the various pulping processes an effort is made to keep their formation to a minimum as far as practicable. Strong hydrolyzing acids convert cellulose to glucose. In treatments of cellulose with acids, alkalies, or other reagents, depending upon the conditions of

hydrocellulose

treatment, a variety of products are possible, ranging all the way from normal or unchanged cellulose to the lowest decomposition products, such as carbon dioxide and water.

Cellulose, in many of its reactions, resembles a trihydroxy alcohol and so forms cellulose alcoholates, esters, ethers, and on oxidation yields aldehydes and acids. Some of the most important esters commercially are the nitrates, formed from cellulose by the action of a mixture of concentrated nitric and sulphuric acids.

Other important constituents of the lignocelluloses are the hemicelluloses. The hemicelluloses include a series of complex polysaccharides about which there is a great deal of argumentation as to the proper definition. Usually, however, they are defined as polysaccharides soluble in dilute alkalies and convertible into simple sugars by heating with dilute acids at atmospheric pressure. Sometimes the definition includes the statement that they should be insoluble in boiling water. This is done to exclude starch and certain other substances that are clearly not related to the hemicelluloses.

The hemicelluloses are anhydrides of hexose and pentose sugars. Xylan, araban, mannan, and galactan give xylose, arabinose, mannose and galactose respectively, on hydrolysis. The hemicelluloses were formerly known as reserve celluloses, the theory being that they were stored against a period of great metabolic activity, such as occurs in the germination of seeds and the renewal of growth in woody plants in spring. It is now

generally believed that they do not serve as reserve materials, although it is held by some that they are consumed when the more readily utilizable carbohydrates are exhausted. The pentosans appear to be structural and not reserve materials in wood where they serve as a cement to hold the fibers together. The hemicelluloses exhibit somewhat the properties of gums and are sometimes called "wood gums".

The hemicelluloses are completely soluble in dilute caustic alkalies. A cold or hot 5 per cent solution of sodium hydroxide is usually employed for their extraction, but pentosans are completely extracted from woods only after protracted treatment with dilute caustic solutions and at the expense of some cellulose. When hemicelluloses are fused with alkalies aliphatic acids and other decomposition products are produced.

Xylan is the most abundant and commonly occurring hemicellulose. It is the anhydride of the pentose sugar, xylose, and has the empirical formula $C_5H_8O_4$. Xylan is dissolved by dilute caustic solutions but can be reprecipitated by the addition of alcohol. Xylan can be converted to xylose by the action of hydrolyzing acids, but the xylose is rather hard to get because of its unstability. Oxidizing acids convert xylan to oxalic and other aliphatic acids. The most prominent characteristic of xylan and other pentosans is the formation of furfural by dehydration when heated with dilute mineral acids. There are appreciable amounts of furfural produced when pentosans are heated with water alone under pressure. Some esters

and ethers of xylan are known, among them the mono- and diacetyl derivatives and the dinitrate. Pure xylan, free from lignin, does not give the methoxyl reaction.

Lignin, the third important constituent of the ligno-celluloses, represents the non-carbohydrate portion of lignified tissue after it has been freed from tannins, resins, fats, and similar minor constituents. There has been a great deal of discussion as to the constitution of lignin owing to the fact that it has not been isolated unchanged. It seems also to lack uniformity when isolated in different ways from various sources.

One of the most prominent characteristics of lignin is that it contains methoxyl and acetyl groups. Hydroxyl groups have also been found but the presence of ketone and aldehyde groups has not been satisfactorily proved. Nitration, chlorination, sulphonation, oxidation, and reduction give either indefinite products, or substances furnishing only questionable information on structure. Lignin is very susceptible to the action of oxidizing agents, and oxalic and other aliphatic acids have been found among the oxidation products. It is quite resistant to the action of strong mineral acids, however, and its isolation depends upon this property; the cellulose being dissolved away with strong sulphuric or hydrochloric acid leaving the lignin undissolved but probably affected to some extent.

Lignin closely resembles the tannins in many of its reactions but no convincing evidence of a cyclic structure has been produced. Lignin is profoundly affected by all methods

employed for its isolation, hence the lignins obtained by the various pulping processes have many different characteristics. The lignin is commonly thought of as the cementing material which holds the blocks of cellulose units together to form the plant structure, but at present it is an unsettled question as to whether the lignin is chemically combined with the cellulose, admixed, or adsorbed. It is an experimental fact, however, that regardless of the way lignin is bound to the cellulose, some of it is held so firmly that it can be completely removed only at the expense of some cellulose, and the remaining cellulose is affected to such an extent that it differs in some degree from the cellulose as it occurs in the plant.

The minor constituents are present only in small per cents, and in some varieties of lignocelluloses certain of these constituents may be almost entirely absent. However, in some cases the presence of a small amount of certain of these constituents may exert such an influence as to profoundly influence the pulps obtained therefrom, and may cause the pulps to be undesirable for certain purposes.

The purpose of the various pulping processes is to free the cellulose fibers from the other constituents as much as is economically practicable. In general no effort is made to remove one constituent at a time, but the processes are carried out so as to remove as much as possible of all of them in one step usually. The physical properties of the resulting cellulose residue are also of equal importance, and must be

given as much weight as the purity of the cellulose.

III - PREVIOUS WORK

COMPOSITION OF THE CORN PLANT

Although there are numerous varieties, there exists only one botanical species of corn, *zea maise*. The mature plant consists of stems, roots, leaves, husks, and ears. The ears consist of the grain arranged upon the cob. The stem is covered on the outside with a hard, flinty rind or shell called the cortex. The inner portion consists of a soft pith traversed longitudinally by numerous fibro-vascular bundles, arranged with the smaller ones thickly placed near the outer edge, and the large ones, less abundant, towards the center.

The outer covering of the stalk is made up of long, thick-walled, slender cells or sclerenchyma fibers. The fibro-vascular bundles are made up of long fibers and vessels or tubes. The pith cells are short, broad, and without much strength. At intervals of 8 to 10 inches along the stalk the fibro-vascular bundles send out branches to the leaves, thus forming by the branching and rejoining of bundles dense, enlarged portions known as nodes. These nodes make up about 26 per cent of the shell proper, or about 6 per cent of the entire plant. The shell, not including the nodes, is about 54 per cent and the pith, 20 per cent, of the stalk. However, because of the light, porous nature of the pith, the percentage by volume is much greater.

The earlier investigations on the chemical constitution of the corn plant were of an agricultural or botanical

nature, and the analyses recorded do not, in general, express the constituents of the corn plant in the same terms as those used by the pulp chemists.

A typical analysis from the agricultural viewpoint is given in the following table. The data are from Schweitzer (32).

Analyses of the Corn Plant

Constituent	: Stems :	Leaves :	Husks :	Whole : Plant
Crude Ash	: 1.55 :	5.22 :	6.23 :	4.50
Ether Extract	: 0.52 :	0.71 :	0.83 :	2.37
Crude Fiber	: 34.75 :	24.42 :	35.87 :	28.29
Crude Protein	: 4.87 :	8.31 :	4.37 :	4.51
Carbohydrates	: 58.31 :	61.34 :	54.80 :	40.33

A more complete analysis on the stalk and one approaching closely to the form used by the cellulose industries is recorded by Wiley (33). It is as follows:

Analyses of the Corn Stalk

Constituent	: Nodes :	Pith of : Internodes:	Shell of : Internodes:	Proportional : Average
Per cent of parts	: 26.08 :	20.25 :	55.67 :	-
Moisture	: 6.52 :	7.01 :	4.95 :	5.77
Crude Fiber	: 37.94 :	41.44 :	46.01 :	42.98
Ash	: 2.11 :	2.80 :	1.94 :	2.16
Fat	: 0.94 :	1.17 :	0.78 :	0.91
Proteids	: 4.38 :	3.50 :	2.44 :	3.16
Carbohydrates (other than fiber)	: 48.21 :	44.08 :	43.88 :	45.04
Digestibility (by artificial digestion)	: 60.05 :	67.70 :	71.12 :	67.55
Solubility in 1.25% H_2SO_4 (1/2 ⁴ hour at 3 atmospheres)	: 44.28 :	54.27 :	37.64 :	42.77

⁴10 grams in 200 c.c. of solution.

Constituent	:Nodes:	Pith of	:Shell of	:Proportional
	:	:Internodes:	:Internodes:	:Average
Solubility in 1% NaOH ^a	:	:	:	:
(atmospheric pressure)	:44.28:	45.74	: 43.12 :	44.24
Solubility in 1% NaOH ^a	:	:	:	:
(at 3 atmospheres pressure)	:51.45:	53.11	: 48.03 :	49.94
Furfural Content	:13.75:	12.98	: 12.56 :	12.94
Xylan	:22.53:	21.29	: 20.60 :	21.22
Reducing Sugar as Dextrose	:28.86:	23.10	: 25.48 :	25.86
Dextrose by Fermentation	: 5.40:	5.40	: 4.80 :	4.55
Cellulose, total	:50.46:	51.97	: 53.44 :	52.44
Cellulose, alpha	:35.12:	33.07	: 40.55 :	37.62

^a10 grams in 200 c.c. of solution.

A recent examination of the tissue of the corn stalk is that reported by Peterson and Hixon (34). Their work was done at about the same time as the work recorded in the next section, and is given here for the sake of completeness. Their results only are given. For a detailed account of their method of attack and procedures used reference should be made to the original paper. All results are calculated on an oven-dry basis.

Determination of Stalk Lignin.

<u>Method</u>	<u>Per Cent</u>
72% sulphuric acid	34.3
Willstatter (fuming hydrochloric acid)	26.2

Analysis of the Cross and Bevan Cellulose.
(45.5 per cent of oven-dry stalk)

<u>Constituent</u>	<u>Per Cent</u>
Pentosan	7.8
Lignin, average	2.0
Ash	0.3
Cellulose (corrected)	35.4

Composition of Cornstalk under Various Analyti-
cal Treatments

(Results in percentage of oven-dry stalk)

	:	:5% NaOH Extract		:	: Acid	
Designation of	:	:Original:of Stalk		:	: Hydrolysis	
Tissue	:	:Stalk	:46.2%	:55.8%	:40.7%	:59.3%
	:	:	:Fraction	:Fraction	:Fraction	:Fraction
	:	:	:(Soluble):	:(not solu-:	:(Soluble):	:(not solu-
	:	:	:	:ble	:	:ble
	:	:Per Cent	:Per Cent	: Per Cent	: Per Cent	:Per Cent
Lignins	:	: 34.4	: 26.5	: 7.6	: 14.3	: 20.0
	:	:	:(by diff.)	:	:(by diff.)	:
Ash	:	: 3.6	: -	: 1.6	: -	: 1.4
Hemicellulose:	:	:	:	:	:	:
Pentosans	:	: 27.6	: 17.3	: 7.1	: 20.8	: 4.1
Hexosans	:	: 1.5	: None	: -	: 4.9	: -
Cellulose	:	:	:	:	:	:
(by differ-	:	:	:	:	:	:
ence)	:	: 33.1	:	: 37.3	:	: 35.8

Analysis of 1% NH₄OH Extract.

	<u>Per Cent</u>
Total solids extracted by 1% NH ₄ OH	6.00
Total sugars (calculated as glucose)	2.17
Pentosans (by furfural)	0.85
Galactans (by mucic acid)	Indefinite trace

Authors' note, "This analysis indicates that the water-soluble hexose carbohydrates, including starch, are not present to more

than about 2.0 per cent of the total stalk."

After extraction with 1% ammonia, the tissue was extracted with 5 per cent sodium hydroxide. The extract was treated with a 1:1 volume of alcohol, and a yellow, amorphous powder precipitated.

Analysis of the Precipitate.

	<u>Per Cent</u>
Moisture (loss at 100° C)	12.2
Pentosan (furfural distillation)	69.5
Lignin (72% sulphuric acid)	15.1
Ash	<u>8.1</u>
Total	102.9
Reducing sugars as xylan (by Fehling)	69.0

The lignins were isolated from the alcoholic solution by distilling off the alcohol and precipitating with acid.

Analysis of the Lignin Fraction

	<u>Per Cent</u>
Moisture (loss at 100° C)	22.0
Pentosans	Indefinite trace
Reducing sugars (hydrolysis)	" "
Lignin (by 72% sulphuric acid)	76.1
Ash	<u>1.0</u>
Total	99.1
Methoxy content	14.0

The lignins were obtained as a light brown, amorphous powder. When suspended in water, they softened at 60° C to a sticky, resinous oil, which soon set on cooling to a brittle, easily pulverized mass.

Comparison of Compositions of the Cortex,
Vascular Bundles, and Pith of the Cornstalk

Constituent	:Outer :Shell :Per :Cent	:Vascular :Bundles :Per Cent	:Pith :Per :Cent	:Total :Cornstalk :Per Cent
Pentosan	: 25.9	: 26.4	: 27.7	: 27.6
Lignin	: 33.5	: 35.2	: 32.0	: 34.3
Cellulose pulp	: 55.9	: 50.2	: 50.1	: 52.6
Pentosans in pulp	: 16.6	: 13.1	: 12.2	: 14.2
Cellulose (by difference)	39.3	37.1	37.9	38.4

Peterson and Hixon were unable to isolate or detect any pectin or pectic acid in the stalk.

IV - ANALYSIS OF THE CORN STALK

The methods used in analyzing the corn stalk for its constituent parts are those generally used by pulp and paper manufacturers to determine the suitability of various woods as raw material for the cellulose industries. An analysis for this purpose is therefore neither concerned to any great extent with the ultimate analysis of the raw material in terms of its carbon, oxygen, hydrogen and other atomic contents, nor are the grouping of the constituents similar to those of the agricultural and plant chemist who in general employ a different method of attack for their own special purposes.

The Forest Products Laboratory of the United States Department of Agriculture has worked out a sequence of analyses which is believed to be at the present time the most useful procedure for determining the relative values of woods as sources of cellulose. These methods of analyses do not determine the constituent groups whose summation give 100 per cent of the material analyzed, for in some cases there is some overlapping. This is due to the fact that at the present time no method of isolating a constituent group is known which does not to some extent affect other constituent groups. In other words the present methods are so drastic and imperfect that in the isolation of one group other groups are resolved to some extent also. This resolution of other groups is due in some cases to the close combination between groups and in other cases to the

lack of sharpness in the methods of isolation. Hence any procedures which give a 100 per cent summation are open to criticism at the present time. However the methods employed are sufficiently accurate to give a very good comparison of the relative values of the various sources of cellulose. In some cases though, while the chemical composition of two or more raw materials may show a marked similarity the physical structures may be so entirely different that one material will be absolutely useless for certain purposes for which the others are acceptable.

In using the methods recommended for woods in studying the composition of corn stalks the foregoing statement as to difference in physical structure should be borne in mind especially as the stalk is composed of three physically distinct parts as far as cell structure is concerned.

The constituents and groups analyzed for in the corn stalks were as follows:

Moisture

Ash

Solubility in:

Cold water

Hot water (boiling)

Ether

1 per cent sodium hydroxide (boiling)

17.5 per cent sodium hydroxide (cold).

Acetic Acid

Nitrogen (Kjeldahl)

Pentosans

Methyl pentosan

Lignin (with 72 per cent sulphuric acid)

Cellulose (Cross and Bevan)

In the Cross and Bevan cellulose:

Pentosan

Methyl pentosan

Alpha cellulose

Beta cellulose

Gamma cellulose

Solubility in 17.5 per cent sodium hydroxide
(cold).

The determinations were made on corn stalks gathered in March after standing in the field all winter. The bale from which the stalks were secured was one of a large number of bales of stalks put up by the Agricultural Engineering Department for the Engineering Experiment Station, Iowa State College. The stalks were slightly dirty but were not washed before being analyzed as it was believed that washing might affect some of the constituents of the plant. From previous analyses made on clean stalks the ash content of stalks was known and the difference in ash contents between the clean stalks and the stalks examined in this work was considered to

be the amount of dirt on the stalks. The stalks were ground to pass an 80 mesh Tyler standard sieve. This degree of fineness is recommended in order that the reagents used may have good penetration and have a large surface on which to react, and yet the fineness is not too great to cause difficulty in filtering.

The results of the analyses are given in the following table. The first column gives the actual results as determined while the second column gives the results recalculated on the assumption that the stalks contained 5 per cent of mechanically held dirt.

Analyses of Corn Stalks.

Results in Percentages of Oven-dry (105°C) Samples.

	Per Cents as Determined	Per Cents Recalculated for 5 Per Cent Dirt Content
Moisture	9.32	9.32
Ash	6.20	5.00
Solubility in:		
Cold water	6.01	5.93
Hot water (boiling)	18.89	18.34
Ether	5.87	-
1% NaOH (boiling)	53.82	52.25
17.5% NaOH (cold)	60.70	58.93
Ash (in hot water residue)	3.24	-
Ash (in 1 per cent boiling NaOH residue)	3.05	-
Acetic Acid	4.36	4.49
Nitrogen (Kjeldahl)	0.53	0.546
Pentosan	27.11	27.95
Methyl pentosan	0.054	0.055
Lignin (with 72% H ₂ SO ₄)	30.36	31.30
Cellulose (Cross and Bevan)	45.68	45.03

	:Per Cents:	Per Cents Recalcu-
	as Deter-	lated for 3 per
	mined	cent Dirt Content
<hr/>		
In the (Cross and Bevan) Cellu-		
lose:	:	:
Ash	: 1.39	: -
Pentosan	: 8.15	: -
Methyl pentosan	: 0.05	: -
Alpha cellulose	: 53.54	: -
Beta cellulose	: 26.35	: -
Gamma cellulose	: 16.57	: -
Insoluble in 17.5% NaOH	: 56.14	: -
(in cold)		
Total Alpha Cellulose		
in stalk	: 23.3	: -
Furfural Yield	: 15.88	: 16.57
Pentose Yield	: 50.80	: 31.75
(theoretical)		
<hr/>		

Discussion of Results

Moisture Content--The moisture content was about the same value as that usually considered to be the equilibrium moisture content or 10 per cent. Stalks stored in a shed or building soon reach an average equilibrium moisture content of 10 per cent but this may be lowered to 5 or 6 per cent after a considerable period of storage. If stored in the open, stalks soon dry out to about 10 per cent moisture content after being wetted by rain or snow. The equilibrium moisture is about the same as for dry wood and is much lower than for woods recently cut or being seasoned.

Ash Content--The ash content of clean stalks is usually considered to be about 3 per cent. The ash from the boiling

water residue was 5.24 per cent but it is probable that the boiling water removed some of the soluble mineral constituents. The ash content is much higher than that of woods which usually does not exceed 0.5 per cent.

Cold Water - Soluble Content--The cold water-soluble constituents in corn stalks are probably composed mostly of gums and tannins and possibly a small percentage is due to some of the soluble mineral constituents of the stalk.

Hot Water - Soluble Content--The hot water-soluble content is much greater than the cold water-soluble content and is probably composed to a large extent of the wood gums or hemicelluloses such as xylen which comprise a large part of the stalk. In woods the hot water-soluble content is but 1 or 2 per cent higher than the cold water-soluble content and in most of the woods used for paper pulp does not exceed 6 to 8 per cent.

Ether - Soluble Content--The ether soluble content is much higher than that of woods except the resinous woods and indicates that there is probably a large amount of fatty or resinous material in the stalk. The ether-soluble content of western yellow pine is 8.52, of Douglas fir 1.02 per cent and of white spruce 1.36 per cent.

One Per Cent NaOH - Soluble Content--The alkali-soluble extract consists mostly of tannins, resin acids, hemicelluloses and lignins, with slight traces of cellulose. This determination using finely divided material is somewhat com-

parable to pressure cooks made on larger pieces using higher concentrations of alkali.

17.5 Per Cent NaOH - Soluble Content--This determination when made in the cold is somewhat similar in its action to that of the boiling one per cent solution but is not quite as drastic.

The same constituents are removed in about the same degree as with the weaker boiling solution.

These determinations remove from two and one-half to three times as much material from the stalks as from the common pulp woods which average from 15 to 20 per cent alkali - soluble material. This indicates that stalks are much more easily delignified than are the woods and should give about 40 per cent yields of cellulose pulp under conditions much less drastic than those needed in the case of woods.

Acetic Acid Content--The acetic acid content is much higher than that of most woods and is comparable to the acetic acid content of the woods used for destructive distillation. The acetic acid resulting from this determination comes mostly from the acetyl groups present in lignins of the stalks. Destructive distillation of the stalks also causes some formation of acetic acid by resolution of the cellulose while not all the acetyl groups appear in the form of acetic acid. However the high value obtained in this analysis indicates that corn stalks should be a very satisfactory raw material for destructive distillation. Previous studies on corn stalks verify this fact.

Pentosan Content--The pentosan content of corn stalks is much higher than that of any of the pulp woods. This high pentosan value of the stalk causes it to be classed as a pento-cellulose rather than as a ligno-cellulose. The pentosan in stalks is believed to consist almost entirely of xylan. Soft woods average about 8.4 per cent pentosan content while hard woods average 17.5 per cent. Some of the pentosan in the woods is araban but it is usually present in much smaller quantities than is xylan.

Methyl Pentosan Content--The methyl pentosan content of stalks is almost negligible. The methyl pentosan is determined by washing the phloroglucinol precipitate with alcohol and the per cent loss of the furfural phloroglucide calculated to pentosan is termed the methyl pentosan content. There is much doubt about the meaning of this determination and some authorities regard it as worthless. By others the procedure is thought to indicate how much of the pentosan occurs as methyl pentosan in the stalks. Sometimes the amount of alcohol soluble phloroglucide is taken as an index of the formation of phloroglucinol precipitants such as furfural from oxycellulose present in the material. At any rate the low value for stalks indicates that xylan is probably the only furfural forming constituent present in appreciable amounts.

Lignin Content--By lignin is meant the non-carbohydrate portion of the stalk after extraction of the fats, oils, and

resins with benzene-alcohol mixture. Lignins are usually estimated by dissolving out the cellulose and hemi-celluloses with strong mineral acids. The methods of isolating the lignins are not sharp and there is a great deal of argumentation as to their utility. Soft woods in general have a somewhat higher lignin content than the hard woods but there is no marked distinction between the two classes. The lignin content of the soft woods is usually from 27 to 30 per cent while the content of hard woods is usually from 23 to 25 per cent. On this basis the stalks more nearly resemble the soft woods as the lignin content is quite high.

Cellulose Content--The cellulose content was determined by the modified Cross and Bevan method and is the residue left after the alternate chlorination and sodium sulfite extraction had been carried out until the sodium sulfite filtrate remained colorless. The coloration of the sodium sulfite solution is due to lignin present so treatment continued until the color does not appear should mean freedom from lignin.

Actually however the cellulose obtained by chlorination is not pure. It usually contains about one per cent of lignin and some pentosan. It seems to be impossible to bring the pentosan content down to a low value by chlorination. The cellulose obtained by chlorination is usually called total cellulose. The total cellulose content of the pulp woods is from 10 to 15 per cent higher than for corn stalks but in some

of the poorer kinds of wood like the incense cedar and balsa the cellulose content is about the same as that of corn stalks.

Because of the impurities present in the total cellulose it is usually analyzed for the following constituents; ash, pentosans, methyl pentosans, and lignins. To obtain an idea as to the nature of the total cellulose it is usually analysed for alpha-, beta- and gamma-cellulose.

Pentosans and Methyl Pentosans in Cellulose--The stalk cellulose retains about 8 per cent of its weight of pentosan when isolated by chlorination. The pulp wood celluloses retain about the same per cent as the stalks while the hard wood celluloses retain from 20 to 30 per cent of their weight. Calculated on the basis of the original material the pentosan contents of the soft wood celluloses are from 38 to 56 per cent of the total pentosans, for the hard woods 57 to 66 per cent while for corn stalks the content is only about 10 or 11 per cent of the total pentosans. This indicates that the chlorination method of isolation has more effect on the stalk pentosans than it does on the wood pentosans or it would indicate that a large part of the stalk pentosans is held rather loosely.

Alpha-Cellulose Content--This determination is of interest to the manufacturers of soda and sulfate pulps and cellulose derivatives, as alpha-cellulose is the most staple cellulose. Alpha-cellulose is also sometimes called normal cellulose and some authorities such as Heuser (26) consider pure alpha-cellulose, regardless of the source, to be identical with cotton

cellulose. This is a much disputed point however and it is probably best at the present state of cellulose chemistry to define alpha-cellulose as that portion of the total cellulose which will withstand the mercerizing process, or in other words treatment with 17.5 to 20 per cent sodium hydroxide in the cold.

The total cellulose is almost free of lignin and the strong alkali removes almost all of the residual pentosans and degraded celluloses which may be present, such as oxycellulose, so the residue except for ash is quite pure. However alpha-cellulose, even that obtained from cotton, is affected by a second alkaline treatment and in the case of that from woods may lose 4 to 7 additional per cent. For this reason the determination of alpha-cellulose has become rigidly standardized so that comparable results may be obtained from analyses of various cellulose materials.

The alpha-cellulose content of the stalks is about 10 to 15 per cent lower than that of the common pulp woods which vary from 35 to 40 per cent. The total cellulose content of the pulp woods vary from 50 to 60 per cent of the oven-dry material of which 50 to 70 per cent is alpha-cellulose.

Beta- and Gamma-Cellulose Content--The precipitate obtained on acidifying the alkaline filtrate from the alpha-cellulose is the beta-cellulose and the portion remaining in solution is the gamma-cellulose. There is some question as to just what is meant by these determinations. By some it is con-

sidered that there are several cellulose complexes present in the tissue and that they vary in their resistance to chemical reagents, hence the beta- and gamma-cellulose contents represent the amounts of the weaker celluloses present. Others hold that the beta- and gamma-celluloses represent degradation products of the normal cellulose which alone is present in the original tissue. Thus it is possible by oxidation or hydration to convert some of the normal cellulose to oxycellulose or hydrocellulose and these forms, being less resistant than that part of the normal cellulose remaining unchanged, dissolve in the strong alkali solution; also, depending upon the conditions of treatment, oxycelluloses, or other degraded cellulose, of varying powers of resistance can be produced some of which reappear when the filtrate is made acid, while others more degraded still remain in solution. In other words the resolution of normal cellulose is not a step by step process but is a continuous process in which all the substances from normal cellulose itself to its lowest degradation product may be present in the same mixture. For this reason the beta- and gamma-cellulose determinations are of no particular value and are only made in special cases.

In the case of practically all woods the gamma-cellulose content is much higher than the beta-cellulose content whereas in the case of stalks the reverse is true. This discrepancy may indicate some fundamental difference in the nature of wood and stalk cellulose that would merit further investiga-

tion although it is well to bear in mind that in general the relative amounts of the beta- and gamma-celluloses present depend to a great extent on the previous treatment of the tissue.

The analyses made on the cornstalk show that its lignin and pentosan contents are higher than those of woods commonly used for pulp and paper manufacture, and both its total cellulose content and alpha-cellulose content are lower than those of the woods. Hence a lower yield of pulp of the same degree of purity can be expected from stalks. On the other hand the analyses indicate that stalks are more easily delignified than are woods, or in other words that a cellulose pulp of equal purity can be obtained with less drastic treatment. The chemical composition of the stalk is sufficiently similar to pulp woods to make it a possible source of cellulose but differences in physical structure, which these analyses do not bring out, may cause technical difficulties which the chemical analyses would not justify.

Analytical Methods

Moisture--The sample weighing 3 to 4 grams is placed in a weighing bottle and dried in an oven at 105°C until no decrease in weight takes place. This usually requires 4 to 6 hours. The weighing bottle should be closed while it is cooling in the desiccator.

Ash--Two or three grams of the stalk are incinerated in a platinum dish in an electric muffle furnace at a dull-red

heat. The ash is stirred at intervals with a platinum wire to insure complete combustion.

Cold - Water - Soluble--Two grams of stalk powder, 80 to 100 mesh, are placed in a 400 c.c. beaker, 300 c.c. of water added, and allowed to digest at room temperature with frequent stirring for 48 hours. The stalk is then transferred to a tared alundum crucible, washed with cold water, dried, and weighed in a weighing bottle.

Hot - Water - Soluble--Two grams of stalk powder are digested with 100 c.c. of water in a 500 c.c. Erlenmeyer flask provided with a reflux condenser. After boiling gently for 8 hours, the stalk is transferred to a tared alundum crucible, washed with hot water, dried, and weighed. The loss in weight represents the portion soluble in hot water.

Alkali - Soluble (17.5 per cent NaOH)--One gram of the stalk powder is placed in a 250 c.c. beaker, 25 c.c. of 17.5 per cent sodium hydroxide solution added and mixed thoroughly with a glass rod, then the beaker is covered with a watch glass and the contents let stand 30 minutes. Dilute with 25 c.c. of water and filter through a tared alundum crucible. Wash the residue with 50 c.c. of 8 per cent sodium hydroxide solution, then with water, 1 per cent acetic acid, and finally with water until the filtrate is neutral to methyl red. The crucible is then dried and weighed.

Alkali - Soluble (1 per cent NaOH)--Two grams of the stalk powder are placed in a 250 c.c. beaker and 100 c.c. of a

1 per cent solution of sodium hydroxide added. The beaker is placed in a bath of boiling water, covered with a watch glass, and with occasional stirring, left for 1 hour. The stalk is filtered off, washed with hot water, dilute acetic acid, and water, dried, and weighed.

Ether - Soluble--A sample of 2 or 3 grams of dry stalk powder is extracted with ether in a Soxhlet extractor for 6 hours. The solvent is driven off and the residue in the extraction flask dried and weighed.

Acetic Acid--Two grams of stalk powder are placed in a 250 c.c. Erlenmeyer flask and 100 c.c. of 2.5 per cent sulphuric acid solution added. The flask is connected with a reflux condenser. The contents are boiled gently for three hours and allowed to cool. The interior of the condenser is washed down with a little distilled water and the contents of the flask are transferred to a 250 c.c. graduated flask. Distilled water free from carbon dioxide is added up to the mark, the solution allowed to stand several hours with frequent shaking, and then filtered.

A wide-mouthed, round-bottomed, 750 c.c. flask is provided with a rubber stopper containing: (1) a dropping funnel; (2) a glass tube drawn out to a capillary, closed with a rubber tube and pinchcock, and extending to the bottom of the flask; and (3) a Soxhlet connecting bulb tube. An ordinary condenser is used, to the end of which is attached for a receiver a 500 c.c. distilling flask cooled with a stream of

water and connected with a Manometer and suction pump.

A few pieces of pumice are placed in the boiling flask, to which is added 200 c.c. of the filtrate obtained above. The flask is heated in an oil bath maintained at 85°C , while the pressure is reduced to 40 to 50 millimeters. When the contents of the flask reach about 20 c.c., distilled water free from carbon dioxide is added through the dropping funnel, drop by drop, at the same rate that distillation takes place. When 100 c.c. of wash water have been distilled over, the distillate is titrated with 0.05 N sodium hydroxide, using phenolphthalein as the indicator. The number of c.c. of sodium hydroxide used is multiplied by $5/4$ and calculated as acetic acid.

1 c.c. of 0.05 N $\text{NaOH} = 0.0050$ gram $\text{CH}_3 \cdot \text{COOH}$.

The acetic acid contains some formic acid. This may be determined, and the correction applied, by adding an excess of a saturated solution of mercuric chloride to the neutralized, concentrated distillate and heating on the water bath for 2 hours. The mercurous chloride formed by reduction is filtered off in a Gooch crucible, washed, dried at 100°C and weighed. The weight of mercurous chloride multiplied by 0.0975 gives the weight of formic acid.

Nitrogen--Place 5.5 grams of the stalk powder in a Kjeldahl flask of 550 c.c. capacity, add 10 grams of pure anhydrous sodium sulphate, 0.5 gram of crystalline copper sulphate and 25 grams of concentrated sulphuric acid. Place the

flask in an inclined position and heat below the boiling point of the acid until frothing has ceased. Then increase the heat until the acid boils briskly and digest for a time after the mixture is colorless or nearly so, or until oxidation is complete.

After cooling, dilute with 200 c.c. of water, add a few pieces of pumice stone, and then, with careful cooling, sufficient (60 c.c.) of a saturated solution of sodium hydroxide to make the solution strongly alkaline. Pour the alkali down the side of the flask so that it does not mix at once with the acid. Connect the flask immediately with a Kjeldahl bulb attached to a condenser. The tip of the condenser is provided with an adapter in contact with the bottom of a vessel containing 50 c.c. of 0.1N hydrochloric acid and 0.5 c.c. of methyl red indicator. Mix the contents of the Kjeldahl flask by agitation, then heat until 150 c.c. have distilled over. Titrate the distillate with 0.1N sodium hydroxide and calculate the nitrogen.

A blank should be run, using 3.5 grams of cane sugar, and a correction applied if necessary. The nitrogen multiplied by 6.25 gives the protein.

Pentosans--Place 1 or 2 grams of the stalk powder in a 250 c.c. flask provided with a separatory funnel and an outlet tube, the connection with the flask being of ground glass. Attach the outlet tube to a condenser. Add 100 c.c. of 12 per cent hydrochloric acid (sp. gr. 1.06) and distill at the rate

of 30 c.c. in 10 minutes. Pass the distillate through a small filter before entering the receiver. As soon as 30 c.c. of distillate are collected, add 30 c.c. of hydrochloric acid to the flask, and continue the distillation in this manner until the distillate is free from furfural. All of the furfural is usually obtained in the first 270 c.c. of distillate. As long as furfural is formed, the distillate will give a pink color when a drop is allowed to merge with a drop of aniline acetate on filter paper. Add 40 c.c. of filtered phloroglucinol solution to the distillate, and make up to 400 c.c. with hydrochloric acid. The solution soon turns greenish black and furfural phloroglucide precipitates. After standing 16 hours, test the supernatant liquid with the aniline reagent. If a pink color is obtained add more phloroglucinol and let stand several hours longer.

Filter through a tared Gooch crucible with a thick asbestos mat, taking care that the crucible is always partially filled with liquid. Wash with exactly 150 c.c. of water, dry in an oven at 105° C. for 4 hours, transfer to a weighing bottle, cool in a desiccator and weigh. The precipitate is hygroscopic.

The crucible is placed in a narrow beaker and 20 c.c. of 95 per cent alcohol added. The beaker is then placed for 10 minutes in a water bath maintained at 60° C. The alcohol is removed with a suction pump and the process repeated (usually 4 or 5 times) until the alcohol that runs through is practically

colorless. Pure furfural phloroglucide is not entirely insoluble in alcohol. Each extraction removes about 0.014 gram. The crucible is again weighed when dry and the furfural phloroglucide calculated to furfural or pentosan by Krober's tables or formulae. The soluble phloroglucides are usually calculated to methyl pentosan.

Furfural, pentose, or pentosan is calculated from the weight, a, of furfural phloroglucide. In the formulae given below, the factor 0.0052 represents the amount of phloroglucide remaining dissolved in the hydrochloric acid. From a weight of phloroglucide

Under 0.03 gram:

$$\text{Furfural} = (a + 0.0052) \times 0.5170$$

$$\text{Pentoses} = (a + 0.0052) \times 1.0170$$

$$\text{Pentosans} = (a + 0.0052) \times 0.8949$$

Between 0.03 and 0.30 gram:

$$\text{Furfural} = (a + 0.0052) \times 0.5185$$

$$\text{Pentoses} = (a + 0.0052) \times 1.0075$$

$$\text{Pentosans} = (a + 0.0052) \times 0.8866$$

Over 0.3 gram:

$$\text{Furfural} = (a + 0.0052) \times 0.5180$$

$$\text{Pentoses} = (a + 0.0052) \times 1.0026$$

$$\text{Pentosans} = (a + 0.0052) \times 0.8824$$

Methyl pentosan--The methyl pentosan determination is given in the preceding determination of pentosans. The methyl pentosan determination is usually omitted as there is some ques-

tion as to its value.

Lignin--Place an acid-treated, tared alundum crucible containing 2 grams of stalk powder in a Soxhlet apparatus which is so filled with glass beads that the top of the crucible will project above the siphon. Extract the stalk with alcohol-benzene mixture for 6 hours, dry by suction, wash thoroughly with hot water, and dry in the oven. Carefully transfer the stalk with a brush to a 100 c.c. beaker, add 30 c.c. of 72 per cent sulphuric acid, and mix thoroughly with a glass rod. Let stand in a desiccator with frequent stirring for 18 hours. If free from cellulose, transfer to a 1.5 liter beaker and dilute to 1200 c.c. Cover with a watch glass and boil gently for 2 hours. Maintain the original volume by occasional addition of hot water. Allow the contents of the beaker to cool and settle, siphon off the clear liquid, and filter off the lignin. Wash with cold or warm water until the filtrate is neutral; dry, and weigh. Transfer the lignin that can be easily removed to a tared platinum dish, incinerate, determine the percentage of ash, and apply the correction.

After standing in the acid 18 hours, a portion of the lignin should be tested for freedom from cellulose by staining with iodine-sulphuric acid reagent.

Cellulose--Two grams of stalk powder held in a tared alundum crucible are extracted with alcohol-benzene mixture (32 parts of alcohol and 68 parts of benzene) for 6 hours, dried by suction, and washed with hot water. The moist sample is then

transferred to a Gooch crucible with a fixed perforated bottom. Suction is applied while the sample is being transferred by means of a jet of water from a wash bottle. After the transfer, the water in the suction flask is sucked through the sample several times in order to secure any fine particles that might have gone through the perforated bottom at the start.

An inverted Gooch crucible holder is next fitted over the Gooch crucible so as to make air tight contact all around by means of the rubber tubing. The holder in which the crucible rests is removed from the suction flask and connected by rubber tubing to a chlorine gas train. The apparatus is firmly supported by clamps and ringstand. The stem of the inverted Gooch crucible holder is then connected to a water pump and washed chlorine gas is sucked up through the moist sample for 5 minutes at the rate of about 40 bubbles per minute.

The inverted crucible holder is then removed, suction is applied to the bottom holder and the residue is washed first with sulphur dioxide water to remove the excess chlorine and then with cold water. The residue is washed into a 250 c.c. beaker using 2 per cent sodium sulphite solution and enough excess is added to make 100 c.c. The beaker is held in a boiling water bath for 30 minutes, the contents filtered, washed, and again chlorinated. This operation is repeated until the chlorinated material fails to give a pink color when the sodium sulphite solution is added. Stalks require about 5 chlorinations.

The cellulose is finally bleached by adding 20 c.c. of 0.1 per cent potassium permanganate solution, allowing to stand 10 minutes, and rendering colorless with sulphur dioxide water. It is then filtered, washed, returned to the beaker, 200 c.c. of water added, and heated on the steam bath with occasional stirring for 2 hours. The cellulose is filtered, washed with hot water, alcohol, and ether, and dried in the oven at 105° C. for 2 hours. After weighing, the ash content is determined by incineration.

Alpha-cellulose--One gram of oven-dry cellulose obtained by chlorination is triturerated for 30 minutes with 25 c.c. of 17.5 per cent sodium hydroxide solution. The alkaline solution is separated from the alpha-cellulose by filtration either through an alundum, Gooch, or Jena fritted glass crucible using suction. The alpha-cellulose is then loosened with a glass rod and is washed with a 4 per cent sodium hydroxide solution and then with approximately 500 c.c. of cold distilled water added in small quantities. The alkali insoluble or alpha-cellulose is removed from the alundum crucible with a pointed glass rod and is placed in a 250 c.c. beaker. The filtrate is used for the determination of beta- and gamma-celluloses.

The alpha-cellulose is dissolved in approximately 30 c.c. of 72 per cent (by weight) sulphuric acid, is transferred to a 100 c.c. graduated flask by washing successively with portions of the acid, and is filled with acid to the graduation mark. A 10 c.c. sample is pipetted into a 250 c.c.

pyrex beaker, to which is added 10 c.c. of standard dichromate solution and approximately 60 c.c. of a solution not stronger than 72 per cent (by weight) of sulphuric acid. The oxidizing mixture is boiled gently for exactly five minutes, is cooled in ice, and the excess dichromate is titrated with ferrous ammonium sulphate solution.

The percentage of alpha-cellulose in the oven-dry sample of cellulose is calculated as follows:

$$\frac{10 \times \frac{X - Y}{X} \times 10 \times Z}{\text{Oven-dry weight of sample}} \times 100 = \text{percentage of alpha-cellulose.}$$

Where X is the volume in c.c. of Mohr's salt solution equivalent to 10 c.c. of potassium dichromate solution; Y is the volume in c.c. of Mohr's salt solution used in the back titration of a 10 c.c. aliquot or one-tenth of the original solution of alpha-cellulose dissolved in 72 per cent sulphuric acid; Z is the weight in grams of cellulose oxidized with 1 c.c. of dichromate solution.

Beta- plus Gamma-cellulose--The 350 c.c. of alkaline filtrate containing the beta- and gamma-celluloses, remaining from the insoluble or alpha-cellulose determination, is diluted to exactly 400 c.c. This solution is divided into two equal parts. One 200 c.c. portion, which is left alkaline, is diluted to 250 c.c. in a graduated flask and is used for the determination of the beta- plus gamma-celluloses. A 25 c.c. portion of this solution is pipetted into a 250 c.c. beaker. To it is add-

ed 5 c.c. of the standard dichromate solution and 60 c.c. of 72 per cent sulphuric acid. The contents of the beaker are boiled for exactly five minutes, are cooled in ice, and are titrated as described under the alpha-cellulose determination. From this titration the sum of the percentages of the beta- and gamma-celluloses is calculated as follows:

$$\frac{5 \times \frac{B - A}{E} \times 20 \times 2}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of beta- plus gamma-celluloses.}$$

Where B is $\frac{N}{2}$ or c.c. of Mohr's salt solution equivalent to 5 c.c. of the dichromate solution; A is the c.c. of Mohr's salt solution used in the back titration of one-tenth of the alkaline solution of beta- and gamma-cellulose.

Gamma-cellulose--The remaining 200 c.c. of the alkaline filtrate from the alpha-cellulose determination is acidified with a 10 per cent sulphuric acid solution using one drop of dilute methyl orange as an indicator, adding 5 c.c. of this acid in excess and diluting to 250 c.c. in a graduated flask. This procedure almost immediately precipitates the beta-cellulose. The flask is allowed to stand several hours, until the beta-cellulose coagulates and settles to the bottom. A 25 c.c. portion of the supernatant liquid is pipetted from the flask and is treated as described under the determination of beta-plus gamma-celluloses. From this determination the percentage of gamma- or soluble cellulose is calculated as follows:

$$\frac{5 \times \frac{B - G}{B} \times 20 \times Z}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of gamma-cellulose.}$$

Where B is $\frac{X}{2}$ or c.c. of Mohr's salt solution equivalent to 5 c.c. of the dichromate solution; G is the c.c. of Mohr's salt solution used in back titration of gamma-cellulose.

Beta-cellulose--The percentage of beta-cellulose is obtained by subtracting the percentage of gamma-cellulose from that of the beta- plus gamma-celluloses.

Standard Solutions for the Alpha-, Beta-, Gamma-Cellulose Determinations.

Theoretically, cellulose is decomposed as follows upon oxidation with potassium dichromate in sulphuric acid solution:



Ninety grams of chemically pure potassium dichromate are dissolved in one liter of distilled water.

One hundred fifty-nine and nine-tenths grams of chemically pure ferrous ammonium sulphate (Mohr's salt) are made up to one liter with distilled water, containing 10 c.c. of 10 per cent sulphuric acid to prevent hydrolysis and avoid the separation of the basic salts.

The potassium dichromate solution is standardized against either Cross and Bevan cellulose obtained from wood pulp, or cotton.

Approximately one gram of cellulose (not corrected

for ash) dried to constant weight at 105°C is taken from a weighing bottle and placed in a 250 c.c. beaker. This is triturated with 50 c.c. of 72 per cent sulphuric acid and allowed to stand until solution is complete. The sulphuric acid solution is transferred to a 100 c.c. graduated flask. The beaker is washed several times with 72 per cent sulphuric acid to insure complete removal of the dissolved cellulose. The flask is filled to the graduation mark with 72 per cent sulphuric acid and the contents are thoroughly mixed. To a 10 c.c. portion of the dissolved cellulose pipetted into a 250 c.c. beaker, 10 c.c. of potassium dichromate solution and approximately 60 c.c. of 72 per cent sulphuric acid are added. The solution in the beaker is boiled for exactly five minutes, is cooled in ice, and is titrated with ferrous ammonium sulphate solution using potassium ferricyanide as the indicator. The titration is conducted in the usual way and the point where a deep of the titrated solution gives a blue color with a drop of the indicator is taken as the end point of the titration. The relative value of the ferrous ammonium sulphate solution to the dichromate solution is established by titrating a 10 c.c. portion of potassium dichromate solution with ferrous ammonium sulphate solution, using potassium ferricyanide as the indicator. From these values the cellulose equivalent of the dichromate solution is calculated as follows:

$$\frac{\text{Weight of cellulose taken}}{\text{c.c. dichromate used in oxidation}} = \frac{\text{Grams cellulose per c.c. of dichromate solution}}{= 2.}$$

V - ISOLATION OF CORE STALK CELLULOSE WITH ALKALIES

At the present time practically all of the soft, easy-bleaching pulps used for the manufacture of high-class book, magazine, general printing, and the cheaper writing papers are made by the soda process. In England such pulps are produced from esparto or Spanish grass; in America, from the poplars and similar woods. Although the soda process of wood-pulp manufacture is not employed commercially to so great an extent in America as the sulphite and mechanical processes, it is well adapted for producing pulp fibers from any kind of wood or other fibrous vegetable material, no matter how resistant to chemical attack it may be.

At the present time, also, pulps with a high percentage of alpha-cellulose are becoming more important in the industries for special purposes. Among the cellulose industries requiring high alpha pulps are the rayon industry, especially those plants using the viscose process which takes a tremendous tonnage annually, and the various nitrocellulose processes. In general the pulps produced by the various pulping methods are not high enough in their alpha-cellulose content to be used without further purification and the soda process or digestion with other alkali salts is very often used as a supplementary process to secure the high alpha pulps.

The purpose of the experiments recorded in this section of the thesis was to study some of the factors in the iso-

lation of corn stalk cellulose with alkalies, mainly sodium hydroxide and sodium carbonate. The primary object was to secure information on the chemical nature of stalk cellulose and the chemical reactions which occur when the alkalies react with stalks rather than to determine the physical nature of the pulps secured. For this reason stalk powder was used in the experiments, so that the reagents would have their greatest effect, and the pulps produced were not made into paper and tested for physical properties. However, in most of the procedures the amount of chemical used, the steps in the process, and other essential factors were so selected that they would conform closely with commercial practice.

1. Alkali - Insoluble Cellulose in Cornstalks.

A series of experiments was made to determine how much alkali - insoluble cellulose is present in corn stalks. One gram samples of cornstalk powder passing 60-mesh screen were treated with sodium hydroxide solutions of various concentrations. Each solution, however, held the same amount of solid caustic and the ratio of solid sodium hydroxide to stalks in each case was 5:1.

After this treatment the pulp residues were purified by washing with 4 per cent sodium hydroxide, hot water, 1 per cent acetic acid, and again with hot water. Then the residues were placed in a beaker with 500 c.c. of water and boiled 3 hours. After being filtered, the pulps were washed again with

hot water, dilute acetic acid, and hot water. Next they were dried at 105° C. and weighed. Each residue was then treated with 25 c.c. of 17.5 per cent sodium hydroxide for 2 hours and purified in the same manner as before. The results are given in the following table:

Alkali-Insoluble Cellulose in Cornstalks

	Concentration of Solution					
	2% ^a	5% ^a	10% ^a	15% ^a	17.5% ^b	40% ^a
	Gram	Gram	Gram	Gram	Gram	Gram
Weight of residue	0.3916	0.4005	0.3910	0.3505	0.4055	0.3650
	Following treatment of first residues with 17.5% NaOH					
Weight of residue	0.3380	0.3455	0.3360	0.3305	0.3730	0.3400
Less lignin	0.0235	0.0305	0.0305	0.0485	0.0349	0.0280
Less ash	0.0075	0.0050	0.0105	0.0060	0.0046	0.0060
Weight of cellulose	0.3070	0.2800	0.2950	0.2760	0.3335	0.3060
Cellulose yield (cor. : for 9% moisture)	34.50%	31.10%	29.45%	30.65%	37.10%	34.00%

^aBoiled 2 hours under reflux.

^bTreated 2 hours in cold.

2. High Alpha-cellulose Pulps from Soda Cooks.

The next experimental work was divided into two parts. In the first, it was desired to ascertain if a pulp yielding a high percentage of alpha-cellulose could be prepared by a single treatment, using dilute solutions of sodium hydroxide and a relatively low ratio of caustic to stalks. This treatment of the stalks was carried out at pressures ranging from 25 to 150 pounds. In the second part of the experimental work, the pulp was prepared by a double hydrolysis. It was first given a rather mild treatment at a low pressure, and then subjected to a strong alkali hydrolysis at atmospheric pressure.

Sodium hydroxide, sodium carbonate, and a one to one mixture of the two were used in the double cooks.

The experimental work was further divided into five series of runs, series A, B, C, and D receiving the single treatments, and series E receiving the double hydrolysis.

In series A, twenty-four runs were made, using from 1% to 6% sodium hydroxide and pressures ranging from 25 to 150 pounds. It was desired to ascertain the relative importance of the concentration of the sodium hydroxide as compared to the pressure at which the hydrolysis was carried out. The gage pressures used were 25, 50, 100, and 150 pounds, six different runs being made at each pressure. All of these cooks were six hours long; 10 grams of stalks (air dry) and 50 c.c. of solution being used in each. An outline of the six runs for each pressure is given in the following table:

Series 1						
Run	:	% Conc.	:	% Ratio	:	% Consistency
No.	:	NaOH	:	NaOH/Stalks	:	Stalks/Sol'n
1	:	1	:	5	:	20
2	:	2	:	10	:	20
3	:	3	:	15	:	20
4	:	4	:	20	:	20
5	:	6	:	30	:	20
6	:	8	:	40	:	20

These runs were made in small capped nipples surrounded by water in an autoclave of the usual type.

Analyses of the Pulps

Weight moisture-free samples--9.294 grams						
Pressure		25		50		
Run No.:	% Conc.	Pulp Yield		Pulp Yield		
	NaOH	Grams	%	Grams	%	
1	1	6.10	65.6	6.10	65.6	
2	2	5.25	56.4	6.30	67.7	
3	3	4.70	51.6	5.90	63.4	
4	4	5.10	54.8	4.50	48.4	
5	6	4.50	46.2	4.40	47.5	
6	8	3.90	41.8	3.70	39.8	

Weight moisture-free samples--9.294 grams						
Pressure		100		150		
Run No.:	% Conc.	Pulp Yield		Pulp Yield		
	NaOH	Grams	%	Grams	%	
1	1	5.50	60.2	5.70	61.3	
2	2	4.90	52.7	4.80	51.6	
3	3	-	-	3.90	41.9	
4	4	4.10	44.1	3.90	41.9	
5	6	3.50	35.5	2.80	30.1	
6	8	2.90	31.2	1.40	15.1	

Moisture content of stalks -- 7.04%.

In series B, two runs were made to ascertain the effect of the length of the hydrolysis. The runs were two and six hours long. These cooks were made in the autoclave itself; 100 grams of stalks (air dry) and 765 c.c. of sodium hydroxide solution being used in each. Both were at 100 pounds pressure.

Series B

Run No.	Length of cook	% Conc. NaOH	% Ratio NaOH/Stalks	% Consistency Stalks/Sol'n
1	2 hours	3.75	30	13.07
2	6 "	3.75	50	13.07

Analyses of the Pulps

Weight moisture-free samples--92.94 grams						
Run:	Pulp Yield	: Alpha-	:	:	:	:
No.:	gm. :	% :	cellu-	: Pentosan	: Lignin	: Ash
:	:	:	lose	:	:	:
1	:36.2 :38.9	:	76.52%	: 14.26%	: 9.88%	: 4.68%
2	:34.7 :37.5	:	75.01%	: 11.63%	: 9.02%	: 6.14%

Moisture content of stalks -- 7.04%.

In series C, four runs were made in a two and one-half inch water tight bomb, which was surrounded by water in the autoclave. These cooks were each two hours long; 25 grams of stalks (air dry) and 125 c.c. of sodium hydroxide solution being used in each.

Series C

Run No.:	Pressure	:	% Conc.	:	% Ratio	:	% Consistency
:	:lbs/sq.in.:	:	NaOH	:	: NaOH/Stalks	:	:Stalks/Sol'n.
1	: 75	:	4	:	21	:	20
2	: 75	:	6	:	32	:	20
3	: 125	:	4	:	21	:	20
4	: 125	:	6	:	32	:	20

Analyses of the Pulps

Weight moisture-free samples--23.24 grams						
Run No. :	Grams	:	% Yield	: % Alpha-	: % Lignin	: % Pentosan
:	: of pulp :	:	:	: cellulose :	:	:
1	: 11.8	:	50.7	: 55.64	: 17.64	: 26.00
2	: 9.9	:	42.6	: 81.13	: 13.22	: 21.92
3	: 11.1	:	47.7	: 70.65	: 25.15	: 19.46
4	: 8.9	:	58.2	: 81.25	: -	: 19.60

Moisture content of stalks -- 7.04%.

The runs in series D were made in an attempt to check the results reported by M. M. Mehta (27). In each of the two runs 5 grams of stalks (air dry) were hydrolyzed with 100 c.c. of 4 per cent sodium hydroxide at 150 pounds gage pressure for one hour. The hydrolysis was carried out in the two and one-half inch bomb as described in series C.

Series D

Run	Pressure	% Conc.	% Ratio	% Consistency
	: atms.	: NaOH	: NaOH/Stalks	: Stalks/Sol'n.
1	: 10	: 4	: 85	: 5
2	: 10	: 4	: 85	: 5

Analyses of the Pulps

Weight of moisture-free samples--4.545 grams					
Run No.:	Pulp Yield			% Alpha-cellulose in pulp	
	: Grams	: %			
1	: 1.6	: 35.2	: 86.40 ^a	: 80.45 ^b	
2	: 1.4 ^c	: 30.6 ^c	: 88.54 ^a	: 82.16 ^b	

Moisture content of stalks -- 9.14%.

^aUncorrected for lignin and ash.

^bCorrected for lignin and ash.

^cThe pulp yield in #2 is less than that in #1 due to a slight loss of pulp on filtering.

The runs in series E were made in an attempt to produce a pulp yielding a high percentage of alpha-cellulose by a process similar to the method outlined in the patent of George A. Richter (28). 50 grams of stalks (air dry) were hydrolyzed

for two hours at 25 pounds pressure with 500 c.c. of sodium hydroxide, sodium carbonate, and a one to one mixture of the two alkalies at three different concentrations. These runs were made in a small autoclave heated in an oil bath.

Two 10 gram portions were taken from the residue of each of the above treatments. Portion a was refluxed for two hours with 100 c.c. of 9.11 per cent sodium carbonate solution, and portion b was refluxed for two hours with 100 c.c. of 9.08 per cent sodium hydroxide solution.

Series E

Run No.:	Treatment	% Conc.	% Ratio	% Consistency
:	:	:Alkali	:Alkali/Stalks	:Stalks/Sol'n.
1	: NaOH	: 2.50	: 25	: 10
2	: NaOH	: 4.75	: 50	: 10
3	: NaOH	: 6.95	: 75	: 10
4	: Na ₂ CO ₃	: 2.47	: 25	: 10
5	: Na ₂ CO ₃	: 4.76	: 50	: 10
6	: Na ₂ CO ₃	: 6.62	: 75	: 10
7	: NaOH	: 2.50	: 25	: 10
8	: Na ₂ CO ₃	: 4.73	: 50	: 10
9	: NaOH	: 6.95	: 75	: 10
	: Na ₂ CO ₃	: 6.62	: 75	: 10

The treatments for portions E_a and E_b taken from the above nine runs are given in the following tables:

Portion E_a

Treatment:	% Conc.	% Ratio alkali/ :Stalks	%Stalks/Sol'n.
Na ₂ CO ₃	9.11	100	10

Treatment is the same for all nine runs.

Portion E_0

Treatment: % Conc.	% Ratio Alkali/Stalks:	% Stalks/Sol'n.
NaOH : 9.08	: 100	: 10

Treatment is the same for all nine runs.

In all of the above series of treatments, stalks of the crop of 1927 ground to pass a 40 mesh Tyler standard sieve were used.

Alpha-cellulose Content
of the Pulps

E_0 Weight moisture-free samples--45.43 grams					
Run No.:	Pulp Yield	% Uncorrected for:		% Corrected for	
:	Gm. :	%	:lignin and ash	:lignin and ash	
1	: 25.0 :	55.1 :	75.75 :	70.00	
2	: 22.8 :	50.2 :	82.20 :	76.29	
3	: 18.6 :	41.0 :	92.83 :	85.05	
4	: 32.9 :	72.5 :	70.97 :	57.27	
5	: 29.5 :	64.5 :	73.26 :	60.51	
6	: 29.5 :	65.0 :	74.45 :	58.35	
7	: 26.3 :	57.8 :	74.90 :	60.45	
8	: 24.6 :	54.2 :	75.79 :	67.19	
9	: 21.9 :	48.3 :	82.18 :	74.51	

Moisture content of stalks--9.14%.

E_2 Weight moisture-free samples--10.00 grams.					
Run No.:	Pulp Yield	% Uncorrected for:		% Corrected for	
:	Gm. :	%	% on	:lignin and ash	:lignin and ash
:	:	:Orig.	:	:	:
:	:	: E_0	:	:	:
1	: 9.5 :	9.5 :	52.3 :	79.75	70.61
2	: 10.0 :	100 :	50.2 :	86.52	78.40
3	: 9.0 :	90 :	36.9 :	91.80	84.00
4	: 9.1 :	91 :	68.0 :	73.65	63.45
5	: 9.6 :	96 :	61.9 :	74.07	65.47
6	: 9.1 :	91 :	59.2 :	73.76	63.71
7	: 9.5 :	95 :	54.9 :	74.06	65.79
8	: 10.0 :	100 :	54.2 :	75.22	68.07
9	: 9.45 :	94.5 :	45.6 :	82.55	74.38

Weight moisture-free samples--10.00 grams					
Run No.:	Pulp Yield			% Uncorrected for:	
	Gm.	%	% on	lignin and ash	% Corrected for
			Orig.		
			E ₀		
1	7.8	78	42.9	94.75	86.20
2	7.3	73	36.6	95.00	86.74
3	6.8	68	27.9	95.27	87.62
4	6.8	68	49.3	92.75	85.20
5	5.8	58	37.4	92.85	84.20
6	7.2	72	46.8	91.55	82.12
7	6.9	69	39.9	94.25	85.93
8	6.8	68	36.8	94.24	86.04
9	7.7	77	37.2	94.70	85.39

The purpose of the experiments in Series A was to compare the effect of increasing concentration of alkali with the effect of increasing pressure or temperature in order to ascertain which was the most important variable. The pulps were not analyzed for their respective lignin, pentosan, and cellulose contents so the interpretation of results in this case is perhaps not as critical as it should be. However, since it is well known that alkalies resolve the lignins and hemi-celluloses much more readily than they do the cellulose the resultant pulp yields can be used as an index of the effect of the variables. In previous analyses made on the stalks it was determined that about 35 per cent of the stalks is pentosan-free cellulose so this figure was used as a criterion of purity, although it must be kept in mind that there is some resolution of the cellulose while it is being freed of its incrustants, the extent of this resolution increasing as the cellulose is

obtained in greater purity.

Considering first the effect of pressure while keeping the other conditions constant it is quite evident from the results that increasing pressure is not so important at the lower pressures, but as the pressure is increased to 100 pounds gage the effect begins to be pronounced. However, even at 150 pounds gage the pulp yield is rather high at the weaker concentrations of caustic indicating that the lignins and pentosans are quite resistant to dilute alkali hydrolysis even at high temperatures. A gage pressure of 150 pounds corresponds to a temperature of about 180°C.

At the lower pressures the effect of increased concentration is to cause a gradual decrease in the yield of pulp but even when the concentration reaches 8 per cent, and the caustic to stalk ratio is 40 per cent the pulp yield is about 40 per cent which indicates that the pulp still retains an appreciable amount of incrustants. At the higher pressures and concentrations pulps of higher purity are obtained but at the expense of high yields. In the experiment in which the most drastic conditions prevailed, that is, a gage pressure of 150 pounds, and a caustic concentration of 8 per cent the residue was radically different from those obtained in the other experiments. The residue in this case was almost colloidal and was so slimy that it was difficult to filter. The yield was only 15 per cent indicating that much of the cellulose had been resolved. The residue closely resembled gelatinized cellulose obtained by long beating.

These results indicate that up to the point where conditions are so drastic that much of the cellulose is attacked the concentration of the caustic is more effective than the pressure or temperature. The results also indicate that to secure a pulp of high purity the concentration of the caustic should be about 6 per cent or more, the ratio of caustic to stalk about 25 to 30 per cent, and the pressure about 100 pounds gage. With a cooking time of 6 to 8 hours it seems evident that a high alpha pulp should be secured under the foregoing conditions. While the pulp purity would be high the yield would be low and for making paper pulp the conditions would perhaps be too drastic as the resultant yield would be uneconomical.

The purpose of the experiments in Series B was to ascertain the effect of the length of the cooking period. The conditions for both cooks were those that gave pulps of high purity in Series A, that is, 100 pound gage pressure, ratio of caustic to stalks 30 per cent, but the caustic concentration was changed to 4 instead of 6 per cent in order to give more fluidity to the mixture and prevent possible charring.

The results show that the longer cook gave a pulp of slightly lower alpha-cellulose content. While the difference was slight it indicates that the cellulose was somewhat attacked during the longer cooking period. It is known that cellulose can be entirely destroyed by very prolonged digestion with alkali solutions and in shorter cooks it is attacked to some extent.

The pentosan content decreased slightly during the longer cooking but there was very little effect on the lignin content. Figured on the basis of the total pentosan present in the raw stalk the pentosans decreased from 27 to 5.5 per cent in two hours but only decreased to 4.5 per cent in four more hours of cooking. In the same manner the lignins decreased from about 34 per cent to about 3.84 per cent in two hours but only decreased to 3.56 per cent in six hours. The cellulose content decreased about 4 per cent in two hours and but 6 per cent in six hours. In two hours therefore about four-fifths of the pentosans and about seven-eighths of the lignins are removed while about one-eleventh of the cellulose is lost.

The results were disappointing as regards the alpha-cellulose content, as it was thought that a 90 per cent or higher alpha-cellulose pulp would be obtained. The yield was good, however, considering the rather drastic conditions which prevailed. The analyses would tend to indicate that a certain fraction of the lignins and hemi-celluloses is quite firmly bound to the cellulose, while the remaining fraction of both constituents is readily removed. The analyses only record the results of two and six hour cooks but it seems evident that the lignin and pentosan contents probably decreased quite rapidly from the start and that the largest portion of both was removed in the first half hour.

The purpose of the experiments made in Series 5 was to study the relative effects of pressure and caustic in obtain-

ing pulps of high alpha-cellulose content. In Series A it was found that a gage pressure of 100 pounds, a 50 per cent caustic to stalk ratio, and an 8 per cent caustic concentration gave pulps of high purity. In Series B it was found that a two hour cooking period was sufficient for the small samples used. Accordingly in Series C a two hour cooking period was used, but the concentrations of caustic were dropped to 4 and 6 per cent while the pressures were varied 25 pounds on either side of 100 pounds in order to find out if consistent results would be obtained. The analyses of the pulps show that the results were quite consistent and in accord with conclusions derived from the two previous series of experiments.

The results show that the concentration of the alkali is more important than the pressure. When the same concentration of sodium hydroxide was used, the pulp yields and the alpha-cellulose content of the pulps were almost the same for both the 75 pound gage pressure and the 125 pound gage pressure experiments. When the pressure was held constant and the concentration of the alkali was increased from 4 per cent to 6 per cent the pulp yield was considerably lower and the alpha-cellulose content of the pulp was much higher for the higher concentration. All the pulps retained appreciable amounts of lignins and pentosans. In the case of the purest pulps, that is those obtained using the 6 per cent caustic concentration, the lignin content was reduced from about 34 to about 5.5 per cent based on the original stalks or about 80 per cent of the

lignin was removed. In the case of the pentosans the reduction was from 27 per cent to about 7.5 per cent, or about 70 per cent of the pentosans was removed. The amount of cellulose removed was low, being but 2 or 3 per cent of the cellulose originally present.

M. M. Mehta (27) reported that almost pure alpha-cellulose could be obtained from ligno-celluloses under the following conditions; hydrolysis at 10 atmospheres pressure (180° C.) for one hour using 100 c.c. of 4 per cent sodium hydroxide solution for each 5 grams of ligno-cellulose material. This amount of caustic solution gives an alkali to stalk ratio of more than 4:5 or 85 per cent which would be entirely out of the question in commercial practice. However, in order to ascertain if high alpha pulps could be secured from stalks by such a procedure the experiments in Series D were performed. The results show that pulps of high alpha-cellulose can be obtained but the alpha-cellulose contents were much below those secured by Mehta using other materials. There was some loss of cellulose as indicated by the pulp yields, and on the whole the results were not much better than those secured using somewhat lower pressures and an alkali to stalk ratio of 50 per cent.

The experiments made so far seemed to indicate that it was impossible to secure a pulp of very high alpha-cellulose content, that is 92 per cent or more, from a single treatment with caustic. Furthermore, when pulps of about 80 per cent alpha-cellulose were secured, the conditions were so drastic

that the yields of pulp were low. For these reasons it was decided to try successive alkali cooks under more moderate conditions and with alkali to stalk ratios that were comparable to those used in commercial practice. It was also decided to try sodium carbonate, which is a cheaper alkali than sodium hydroxide, and also mixtures of sodium carbonate and hydroxide. Richter's patent (28) specified conditions that produced 94 per cent alpha-cellulose pulps from spruce wood and other pulp woods so these conditions were duplicated in the experiments made in Series E. The first cook can be either a soda or a sulphite cook but in Series E only alkali cooks were made. The second cooks were made both with sodium carbonate and sodium hydroxide. The first cooks most nearly duplicating commercial conditions were those in which the alkali to stalk ratio was 25 per cent, but for the sake of comparison runs were also made using 50 and 75 per cent ratios. The consistency in all cases was 10 per cent. The pressure was quite moderate being only 25 pounds gage.

The analyses of the pulps resulting from the first cooks are quite consistent and show clearly that sodium hydroxide used alone is superior to soda ash or to a mixture of the two. The alpha-cellulose content will average about 10 per cent higher when sodium hydroxide is used alone for the first cook. The effect of the hydroxide concentration is quite pronounced. By increasing the hydroxide ratio from 25 to 50 per cent the alpha-cellulose content is increased about 6 per cent and in-

creasing it to 75 per cent increases the alpha content about 10 per cent more. Increasing the concentration of the sodium carbonate has some effect on the pulp yield but almost no effect on the alpha-cellulose content of the pulps. When a mixture of sodium hydroxide and carbonate is used the effect of the hydroxide can be readily seen and it acts about the same as if it were alone at the same concentration.

In order to conform to Richter's procedure it is necessary to use an alkali to pulp ratio of approximately 100 per cent in the second cook but taking the average pulp yield as 50 per cent the alkali ratio is but 50 per cent based on the original stalk. The results show that when sodium carbonate is used for the second cook there is practically no purification of the pulp even when this high ratio of alkali to pulp is used. The experiments were carried out at atmospheric pressure using a reflux condenser. These conditions would closely approximate open kettle cooking on a large scale where the evaporation loss can be made up either continuously or at intervals.

The second cooks using sodium hydroxide gave quite satisfactory results. The pulps obtained by this treatment were all high in alpha-cellulose content regardless of whether they were first treated with caustic soda or soda ash. The pulps from the caustic soda first cooks were somewhat purer after the second cook than were the pulps from the soda ash and mixed alkali cooks. The analyses show that the pulps were all better

than 90 per cent alpha-cellulose when uncorrected for ash and residual lignin. Commercial methods of analysis usually do not correct for lignin and ash so that in the case of the pulps obtained from caustic soda and mixed alkali first cooks, the second treatment with sodium hydroxide produced pulps of purity equal to that of wood pulps (94 per cent alpha-cellulose) produced by a similar procedure. Wood pulps of 94 per cent alpha-cellulose content are one of the most important sources of cellulose in the viscose process of making rayon. When corrected for lignin and ash, however, the purity of the best pulps dropped to about 87 per cent.

The yields were quite good considering the purity of the pulps. In the case of Run #1 the yield of 86 per cent alpha-cellulose (corrected) was about 43 per cent based on the original oven-dry stalk. There was probably a small amount of pentosan present, which was not corrected for, but this pulp yield represents practically all the cellulose present in the original stalk. The residual lignin content is about 5 per cent of the pulp and the ash content is 2 - 3 per cent. This ash is not the ash content of the original stalk, however, for there has probably been some changes brought about by the several treatments experienced.

3. Lignin Removal at Low Pressure.

A series of experiments were carried out at a relatively low pressure (30 pounds gage) using sodium hydroxide solutions of several concentrations to ascertain the extent of

lignin removal. The runs were all made in a small autoclave heated with a steam jacket. 100 grams of stalk ground to pass 40-mesh were used in each run, and the cooking period was 7 hours at 30 pounds gage pressure in each case. The conditions are given in the following table.

Run No.	% Conc. NaOH	% Ratio NaOH/Stalks	% Consistency Stalks/Sol'n.
1	0	-	-
2	0.5	5	10
3	1	10	10
4	2	20	10
5	4	40	10
6	6	60	10

The results are given in the following table.

Weight moisture-free samples--92 grams.					
Run No.	% Conc. NaOH	Pulp Yield		% Lignin	% Lignin Removal
		Grams	%		
1	0	63.66	69.2	31.4	36.0
2	0.5	54.84	59.7	30.7	46.0
3	1	48.60	52.8	23.6	63.3
4	2	41.80	45.5	21.2	71.6
5	4	36.14	39.3	15.4	84.5
6	6	33.69	36.7	12.4	86.6

Moisture content of stalks--8.00%.

These results indicate that after about 80 per cent of the lignins have been removed the remaining portion is removed very slowly. The removal of lignins at low pressures (30#) is almost as great as when high pressures (100#) are used if the concentration of alkali is the same in both cases. In

other words the concentration of the alkali has a much more pronounced effect on the lignins than does the pressure. However, the caustic to stalk ratio can be lowered considerably if high pressures are used and the lignin removal will be just as great as if more caustic was used at lower pressures. The concentration of the caustic in the solutions should be about the same in both cases to secure the same degree of lignin removal. An appreciable amount of the lignins are removed by cooking in water alone.

4. Summary.

The results of the experiments using alkali cooks can be summarized as follows:

(1) About 30 per cent of the stalks seems to be quite resistant to sodium hydroxide.

(2) The concentration of the alkali is a more important variable than the pressure or temperature.

(3) High alpha-cellulose pulps can be obtained using high pressures, a caustic to stalk ratio of 25 to 30 per cent and a solution concentration of 6 per cent.

(4) High alpha-cellulose pulps can be obtained using double alkali hydrolysis at low pressures and temperatures if sodium hydroxide is used for the second cook. Either caustic soda or soda ash can be used for the first cook.

(5) The double hydrolysis gives pulps of greater purity than do high pressure single cooks and the apparatus does not need to be so strongly constructed. On the other hand,

the alkali consumption is considerably greater but this can be offset to some extent by using the cheaper alkali, sodium carbonate, in the first cook. A heat recovery process such as that specified by Richter (28) would probably be necessary in the double treatment process. The pulp yield is somewhat greater in the double cook process and the pulps appear to be better physically. The double cook process for stalks seems commercially feasible for the production of high alpha-cellulose pulps. Modifications of this process using several cooks of increasing alkali concentration would perhaps be as satisfactory or even more so, but no work was done on cooks of this sort.

(6) The removal of lignins and pentosans is quite rapid at first but soon slows down to a very gradual rate of removal.

(7) The greater portion of the lignins and pentosans can be readily removed but a portion of the lignins (about 15 per cent of the original lignins) and of the pentosans (25-30 per cent of the original pentosans) seems to be quite firmly bound to the cellulose and cannot be removed without the cellulose itself being attacked sufficiently to cause a loss of several per cent.

(8) In the soda cooks the lignins are removed somewhat faster and to a greater degree than the pentosans but the difference is not pronounced.

VI - ISOLATION OF CORN SEALE CELLULOSE BY CHLORINATION

The estimation of cellulose in plant materials by the use of chlorine was first reported by Cross and Bevan in 1859. This method was favorably received and ever since that time, with some modifications, it has been the most widely used method of estimating cellulose quantitatively. Although this method seemed to have commercial possibilities it was not adopted on a large scale for the production of pulps because of the high cost of chlorine.

In recent years, however, the use of chlorine as a method of disintegrating plant materials for their cellulose has received much attention and it promises to be one of the most important methods of producing pulps in the future. One of the reasons for this present interest is the comparatively low cost of chlorine which makes the process possible on a commercial scale. Another factor is that this method can be used quite successfully in pulping cereal straws several of which at the present time are attracting much attention as possible sources of cellulose. On account of the form of wood chips it is hard to make chlorine penetrate them but such is not the case with cereal straws due to their different physical structure. Still another reason is that pulping with chlorine produces pulps with properties that make them suitable for use in the viscose process for making rayon. It is stated (29) that at present the wood pulps which are most satisfactory for

viscose production are those made from spruce wood by the bisulphite process. Soda and sulphate pulps are not as suitable because the pulping methods are so drastic and the conditions so severe that the cellulose is attacked quite appreciably and hence it loses some of its power of resistance or chemical inertness.

There are several chlorination processes used at the present time and they are confined almost exclusively to Italy, Spain, and France where cereal straws are employed quite extensively for producing cellulose materials. The De Vains process uses an aqueous solution of chlorine while Cataldi uses gaseous chlorine. The raw material is boiled with alkali before chlorination and the chlorinated derivatives are removed with alkali. The preparation of 100 kilograms of dry pulp from poplar wood by the Cataldi process requires a minimum of 45 kilograms of chlorine and 9 kilograms of sodium hydroxide. The pulp from poplar contains 74 per cent of alpha-cellulose and 21 per cent of beta- and gamma-cellulose.

Chlorine water lends itself to large scale production somewhat better than gaseous chlorine. When gaseous chlorine is used the material must be moist as chlorine has but little effect on dry materials. Wood in the form of chips must be chlorinated under a pressure of 6 atmospheres in order to secure penetration. The usual procedure is to give the wood a preliminary cook with sodium hydroxide or sodium sulphite, so that the wood can be mechanically separated into individual

fibers before chlorinating.

The usual procedure in the De Vains process when cereal straws are used as the raw material is as follows. The raw material is first cut into about one inch lengths and is then cleaned and dusted. Next it goes to the digesters where it is cooked in a caustic solution for 5 or 6 hours at 60 pounds pressure. The proportion of caustic to straw is 8 or 9 per cent and the concentration of sodium hydroxide is 12 to 14 grams per liter. The alkali concentration is therefore so low that no attempt is made to recover the caustic from the cook liquors. The material goes from the digesters to the pulping machines where it is mechanically disintegrated. Next it is washed free from caustic and then it is chlorinated in closed vessels with agitators. Saturated chlorine hydrate from absorption towers is led in continuously and the exhausted solution is drained away continuously. The feed and discharge are so regulated that but little chlorine is wasted. The pulp has a consistency of 5 to 7 per cent in the chlorinating vessels.

After chlorination the excess chlorine and the ketone-chlorides are removed from the pulp by washing with a dilute solution of caustic soda. The pulp is then riffled and screened. The pulp is next bleached with chloride of lime in beaters, washed and dried, and is finished pulp. The available chlorine used in the bleaching process is from 2 to 5 per cent of the weight of the dry pulp.

The Cross and Bevan method of isolating cellulose by

chlorination has always been considered important because the cellulose purified in this manner has been less affected by the reagents than that secured by other methods. In other words the treatment is least drastic for the degree of purity secured. Hence cellulose isolated in this manner has been considered to be cellulose with properties almost unchanged and it serves as a good starting point for the study of the cellulose in ligno-celluloses.

The purification of cellulose by this method depends upon the formation of a compound called lignone chloride by Cross and Bevan. They assigned it the empirical formula $C_{19}H_{18}Cl_4O_9$. This compound is soluble in alkalis and sodium sulphite so the purification consists in alternate treatments of the material with chlorine, to produce lignone chloride, and with sodium sulphite or sodium hydroxide to remove the soluble lignin derivative. Cross and Bevan also gave the material a preliminary purification with hot dilute sodium hydroxide but this treatment is not used at present as it was found to lower the yield of cellulose. In quantitative analyses the fats and resins should be removed first with alcohol-benzene extraction. The cellulose obtained by chlorination is usually purified by alternate chlorination and sodium sulphite digestion until the addition of the sodium sulphite to the pulp produces no pinkish coloration. This color is due to a reaction between lignin and sodium sulphite and absence of the color is presumed to denote freedom of the cellulose from lignin. Usually however there is

a small amount of lignin remaining which can be estimated by treatment of the pulp with 72 per cent sulphuric acid.

In addition to the normal cellulose, the crude cellulose obtained by chlorination usually contains quite an appreciable amount of pentosans which can be determined in the usual way and the correction applied. Other impurities may be present also in small amounts. The normal cellulose present is best determined as alpha-cellulose. The determination of alpha-cellulose in cellulose that has been isolated by chlorination may not afford a true measure of the original alpha-cellulose in the material unless the chlorination is carefully controlled. The temperature must be kept low by circulating cooling water during the chlorination and the chlorination must not be prolonged or there is some loss of alpha-cellulose. Bray and Andrews (30) found that over-chlorination produced an increase in the beta-cellulose content at the expense of the alpha-cellulose and the copper number was also greatly increased showing oxy-cellulose formation. This loss of alpha-cellulose is slight however if the chlorination is not continued over a half hour and it would be important only in commercial scale chlorination, as in quantitative work the chlorinating periods are usually only 3 to 5 minutes long and under these conditions there is no oxy-cellulose formed.

1 - Experimental Work

The purpose of the experimental work was to study some of the changes which occur in the corn stalk while its

cellulose is being isolated by chlorination. It was decided to use chlorine water instead of chlorine gas as it was believed that more intimate contact would be secured in this way when using large samples.

The experimental work consisted of two series of runs. In series A the samples were subjected to only one chlorination of varying length. In series B one sample was subjected to alternate chlorination and sodium sulphite digestion until it was free of lignin. After each chlorination a portion of the sample pulp was removed and analyzed to ascertain what changes had taken place.

The chlorinating apparatus in all cases was a one-half gallon glass butter churn equipped with a wooden agitator thoroughly coated with paraffine to resist the action of the solution. The gaseous chlorine was obtained from a #1 cylinder (110#) and was passed through a glass flowmeter before being led to the bottom of the jar through a glass tube. The glass tube entered through the lid and was bent so as to fit into a corner of the jar out of the way of the agitator. At the bottom of the jar the glass tube was bent again so as to deliver the chlorine near the center. When turned rather vigorously the agitator stirred the entire contents of the jar satisfactorily. Any excess chlorine gas was removed from the jar through another glass tube which projected slightly through the lid and was connected to a water suction pump. The suction maintained was very slight and this tube could have been dispensed with as

some chlorine leaked out through the agitator shaft guide.

Analyses--The following constituents were determined on the chlorinated residues by the procedures given in detail in the section on the analysis of the corn stalk, (Section IV, Part II).

(1) Pentosans, by the phloroglucinol method.

(2) Lignins, with 72 per cent sulphuric acid.

(3) Cross and Bevan cellulose, by continuing the chlorination of one gram samples of the residues until no pinkish coloration was obtained on digestion with 2 per cent sodium sulphite solution.

(4) Pentosans in Cross and Bevan cellulose, by the phloroglucinol method.

(5) Pentosans not in the Cross and Bevan cellulose. This value was obtained by subtracting #4 from #1.

(6) Pentosan free cellulose. This value was obtained by subtracting #4 from #3.

Series A. Run #1.

A 100 gram sample of air dry corn stalks ground to pass 40-mesh was mixed with 1500 c.c. of water in the glass churn and chlorinated for 15 minutes with chlorine gas passing into the mixture at the rate of 275 c.c. per minute. The mixture was stirred continuously with the paddle agitator. This volume of chlorine gas weighed about 11.7 grams but was not completely absorbed. Then the mixture was chlorinated for

another 15 minute period at the rate of 225 c.c. per minute or about 9.6 grams of chlorine for the 15 minutes.

The pulp was washed with SO_2 water to remove the excess chlorine, and then with water to remove the excess SO_2 . The washed pulp was digested with one liter of 2 per cent sodium sulphite solution for one hour. The pinkish coloration was quite pronounced. At the end of the digestion period the pulp was thoroughly washed, and dried at 105°C . The results were as follows:

Weight of oven dry residue = 32.6 grams.

Per cent yield on oven dry basis = 68.1%

Analytical Data

Oven dry residue

Pentosans	36.62%
Lignins	31.85%
G and B Cellulose	53.87%
Pentosans in G and B Cellulose	29.05%
Pentosans not in G and B Cellulose.	7.57%
Pentosan free Cellulose	24.82%

Run #2.

A 100 gram sample of the corn stalk powder was mixed with 1500 c.c. of water in the glass churn and chlorinated for one hour with continual stirring. The first 15 minutes, the rate of chlorine gas flow was 275 c.c. per minute. During the remaining 45 minutes the gas flow was 225 c.c. per minute. The

pulp was digested with one liter of 2 per cent sodium sulphite in the same manner as #1, after the excess chlorine had been removed with SO_2 water. The results were:

Weight of oven dry residue 70.0 grams

Per cent yield on oven dry basis 74.6%

Analytical Data

Oven dry Residue

Pentosans 29.47%

Lignins 26.52%

C and B Cellulose 64.30%

Pentosans in C and B Cellulose 27.66%

Pentosans not in C and B Cellulose .. 1.81%

Pentosan free Cellulose 36.64%

Run #3.

A 100 gram sample of the air dry stalk powder was mixed with 1500 c.c. of water in the glass churn and chlorinated for two hours with continual stirring. The chlorine gas flow for the first 15 minutes was 275 c.c. per minute. For the remaining one hour and 45 minutes the gas flow was 225 c.c. per minute. The treatment of the pulp was the same as in Runs #1 and #2. The results were

Weight of oven dry residue = 66.4 grams.

Per cent yield on oven dry basis = 70.65%

Analytical Data

Oven dry residue

Pentosans	28.40%
Lignins	22.90%
C and B Cellulose	66.15%
Pentosans in C and B Cellulose	18.61%
Pentosans not in C and B Cellulose	9.79%
Pentosan free Cellulose	47.52%

Series B, Run #1.

A 100 gram sample of the stalk powder was mixed with 1500 c.c. of water in the glass churn and chlorinated for 20 minutes. The rate of gas flow into the mixture was 275 c.c. per minute. The batch was stirred continually during the chlorination. The sample was next washed with SO₂ water, with distilled water, and then digested for one hour on the boiling water bath with one liter of 2 per cent sodium sulphite solution. The pulp was then thoroughly washed, and dried at 105° C. The results were as follows:

Weight of oven dry residue = 75.7 grams

Per cent yield on oven dry basis = 80.70%

Analytical Data

Oven dry residue

Pentosans	27.94%
Lignins	29.35%
C and B cellulose	57.30%
Pentosans in C and B cellulose.....	26.93%
Pentosans not in C and B cellulose	1.01%
Pentosan free cellulose	30.37%

Run #2.

70 grams of the oven dry residue from Run #1 was mixed with 1200 c.c. of water in the glass churn and chlorinated for 20 minutes. The rate of gas flow was 225 c.c. per minute. The pulp, after chlorination, was purified as in Run #1. The results were as follows:

Weight of oven dry residue = 57.2 grams

Analytical Data

Oven dry residue

Pentosans	29.67%
Lignins	17.00%
C and B cellulose	76.55%
Pentosans in C and B cellulose	28.25%
Pentosans not in C and B cellulose	1.42%
Pentosan free cellulose	47.50%

Run #3.

50.4 grams of the oven dry residue from Run #2 was mixed with 1000 c.c. of water in the churn and chlorinated for 20 minutes at a gas flow rate of 225 c.c. per minute. The pulp was then purified as before, and oven dried.

Weight of oven dry residue = 43.0 grams.

Analytical Data

Oven dry residue

Pentosans	27.90%
Lignin	18.38%

C and B cellulose	89.90%
Pentosans in C and B cellulose	27.81%
Pentosans not in C and B cellulose	0.09%
Pentosan free cellulose	62.00%

Run #4.

38 grams of the oven dry residue from run #3 was mixed with 800 c.c. of water and chlorinated for 20 minutes. The gas flow rate was 225 c.c. per minute. The pulp was purified as before, and oven dried.

Weight of oven dry residue = 51.4 grams

analytical Data

Oven dry residue

Pentosans	22.40%
Lignins	7.56%
C and B cellulose	95.63%
Pentosans in C and B cellulose	22.56%
Pentosans not in C and B cellulose .	0.02%
Pentosan free cellulose	73.25%

Run #5.

26.4 grams of the oven dry residue from run #4 was mixed with 500 c.c. of water and chlorinated for 20 minutes. The gas flow rate was 225 c.c. per minute. The pulp was purified as before, and oven dried.

Weight of oven dry residue = 25.2 grams

Analytical Data

Oven dry residue

Pentosans	19.92%
Lignins	8.94%
C and B cellulose	92.66%
Pentosans in C and B cellulose	18.78%
Pentosans not in C and B cellulose ...	1.14%
Pentosan free cellulose	73.86%

The results of the two series of experiments are summarized in the following tables for comparative purposes.

Series A

(All results calculated on an oven dry
(105° C) basis).

Run	:Length of chlori- :nation in minutes	:Number of chlori- :nation periods	:% yield of :pulp
1	: 30	: 1	: 88.10
2	: 60	: 1	: 74.60
3	: 120	: 1	: 70.65

Analyses of Series A Pulps
(Results as Secured)

Run:	% Lig- :nin	% C and B: :cellulose	% total :pentosans	% pentosans :in cellulose	% pentosans :not in :cellulose	% pentosan :free :cellulose
0a	: 31.30:	45.03 :	27.95 :	8.15 :	19.80 :	36.88
1	: 31.85:	53.87 :	26.62 :	29.05 :	-2.43 :	24.82
2	: 26.52:	64.30 :	29.47 :	27.66 :	1.81 :	36.64
3	: 22.90:	66.13 :	28.40 :	18.61 :	9.79 :	47.52

Results of quantitative analyses of the corn stalk.

Analyses of Series A Pulps

(Results recalculated to original stalk samples)

Run:	% Lig-:	% C and B:	% total	% pentosans	% pentosans:	% pentosan
:min	:cellulose:	pentosans:	in cellulose:	not in	:free	
:	:	:	:	:cellulose	:cellulose	
0	: 31.30:	45.03	: 27.95	: 8.15	: 19.80	: 36.88
1	: 28.10:	47.50	: 23.45	: 25.60	: -2.15	: 21.90
2	: 19.80:	48.00	: 22.00	: 21.70	: .30	: 26.30
3	: 16.20:	46.70	: 20.05	: 13.15	: 6.90	: 33.55

Series B

(all results calculated on an oven dry (105°C)
basis).

Run	:Length of chlori-:	Number of 20 min-:	% yield
	:nations in	:ute chlorinations:	of pulp
	:minutes	:	
1	: 20	: 1	: 80.70
2	: 20	: 2	: 65.90
3	: 20	: 3	: 56.25
4	: 20	: 4	: 46.50
5	: 20	: 5	: 44.45

Analyses of Series B Pulps
(Results as secured)

Run:	% Lig-:	% C and B:	% total	% pentosans	% pentosans:	% pentosan
:min	:cellulose:	pentosans:	in cellulose:	not in	:free	
:	:	:	:	:cellulose	:cellulose	
0 ^a	: 31.30:	45.03	: 27.95	: 8.15	: 19.80	: 36.88
1	: 29.35:	57.30	: 27.90	: 26.95	: 1.01	: 30.57
2	: 17.00:	75.55	: 29.67	: 28.25	: 1.42	: 47.50
3	: 16.58:	89.90	: 27.90	: 27.61	: .09	: 62.09
4	: 7.56:	95.63	: 22.40	: 22.38	: .02	: 73.25
5	: 8.94:	92.66	: 19.92	: 18.78	: 1.14	: 73.88

^aResults of quantitative analyses of the corn stalk.

Analyses of Series B Pulps
(Results recalculated to original stalk sample).

Run:	Wig-	% C and B:	% total	% pentosans	% pentosans	% pentosan
:	min	:cellulose:	pentosans:	in cellulose:	not in	:free
:	:	:	:	:cellulose	:cellulose	:cellulose
0	: 31.30:	45.03	: 27.60	: 8.15	: 19.80	: 56.88
1	: 23.65:	46.20	: 22.55	: 21.75	: 0.80	: 24.45
2	: 11.22:	49.80	: 19.50	: 18.60	: 0.90	: 31.20
3	: 10.35:	50.55	: 15.70	: 15.65	: 0.05	: 34.90
4	: 3.42:	44.50	: 10.42	: 10.40	: 0.02	: 34.10
5	: 3.97:	41.20	: 8.11	: 8.35	: -0.25	: 52.85

The stalk powder contained 6 per cent moisture.

2 - Discussion of Results

The results obtained in Series A show that as the period of chlorination is extended there is a steady decrease in the lignin content but that the removal is not extremely rapid. The Cross and Beman cellulose, of course, should have an almost constant value but there is a chance for error in the method of analysis in that the end point is rather deceptive. When a sample of the pulp is being chlorinated quantitatively, after several alternate chlorinations and sodium sulphite digestions, the pinkish color due to the reaction of any lignin present with the sodium sulphite becomes extremely faint and an error is possible in the required number of chlorinations. There is always a slight loss of pulp in the mechanical handling incident to the chlorinations, washings, and digestions so one too many chlorinations might bring about a mechanical loss that would cause a difference of one or two per

cent. The average, or constant value for the Cross and Bevan cellulose in stalks should be about 45 per cent.

The total pentosans show a steadily decreasing value but the rate of removal is not very rapid. The pentosan content of the Cross and Bevan cellulose shows a rate of removal comparable to that of the lignin. The low values of the pentosans not in the Cross and Bevan cellulose show that they were removed very rapidly. In the two hour run the relatively low value of the pentosans in the Cross and Bevan cellulose and the large value of the pentosans not in the cellulose were probably due to the hydrolyzing action of the hydrochloric acid which was probably formed in appreciable amount during the long continued chlorination.

The results of the Series A experiments are on the whole somewhat indefinite but they do indicate that pulping by chlorination is a rather slow method of removing the lignins, and that a fraction of the pentosans seem to be about as immune to the treatment as is the cellulose.

The results of the experiments in Series B were more satisfactory. The treatment of the stalk sample in this case was almost identical with the quantitative determination of cellulose except chlorine water was used instead of gaseous chlorine.

The table of analytical results recalculated to the original stalk sample shows the effects of the successive chlorinations more clearly than does the table of results as

secured. The values in the second table were obtained from the values in the first table by multiplying the results as secured by the per cent yield of pulp in the run concerned.

When recalculated in this manner the results show the progressive decrease in the lignin content down to a fairly constant value of about 3.5 per cent. Evidently this fraction or form of the lignin is quite firmly bound to the cellulose and probably can only be removed at the expense of some cellulose. Ritter (31) showed that in the case of wood, specifically red alder and western white pine, there are two forms of lignin. One form occurs in the middle lamella or partition wall between cells, is light brown in color, shows structural form, and has a comparatively high methoxyl content (13.6 per cent for red alder and 10.8 per cent for white pine; the other form, found in the cell wall proper, is darker, is amorphous, and has a low methoxyl content (4.8 per cent for red alder and 4.3 per cent for western white pine).

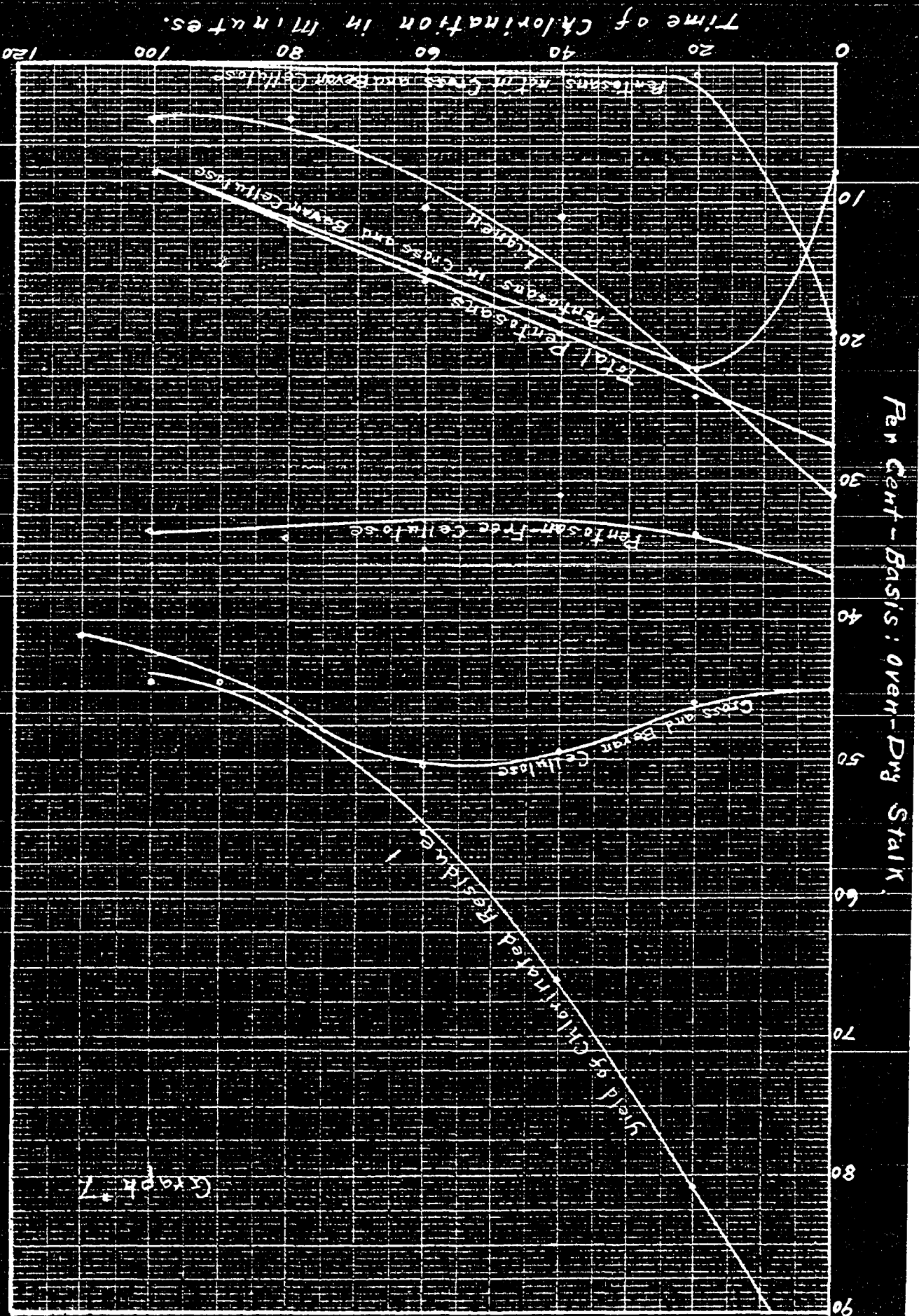
It seems logical to assume then that there are two or possibly more forms of lignin in the stalks; one of which is firmly bound due to its position in the plant structure while the other or others are more easily removed for the same reason. Another possibility is that the reagents used may render a fraction of the lignin more insoluble than the rest. A third assumption is that the lignin in the pith, the cortex and the vascular bundles may differ appreciably from each other. This difference may cause one to be isolated more readily and to a

greater extent than the others.

The values of the Cross and Bevan cellulose, like in Series A, varied somewhat when of course they should have an almost constant value. The differences were probably caused by mechanical losses in handling and by stopping the purification of the analytical samples at slightly different end points. In the third and fourth steps the values are somewhat high and the true values should probably be between 45 and 46 per cent.

The total pentosan values are quite consistent and show a steady but not a rapid decrease down to a constant value of about 8 per cent which agrees very well with the value of 8.15 per cent obtained from quantitative analyses of the stalk. This per cent of pentosan seems to be immune to the effects of chlorination and is evidently either not easily hydrolyzed or is very closely bound to the cellulose.

The values for the per cent of pentosan in the Cross and Bevan cellulose are quite consistent. They show quite clearly that practically all of the pentosan present in the pulp is in the Cross and Bevan cellulose. Of the original 27.6 per cent of pentosan present in the raw stalk about 20 per cent is of an easily hydrolyzable nature while the remaining 8 per cent is as immune to the chlorination treatment as the cellulose itself. Most of the pentosan susceptible to hydrolysis is practically removed in the first step. Furthermore the low values of the pentosans not in the cellulose indi-



cate that the cellulose is not decomposed into furfural yielding substances during the process of isolation by chlorination. This is substantiated by the fact that the pentosan content of the cellulose does not increase as the chlorination progresses.

The pentosan-free cellulose should show an almost constant value of about 36 per cent. In some of the runs this value is a trifle low but in only one case is the error very large. This is in Run #1 where the low value of about 25 per cent was obtained. The pentosan free cellulose value is obtained by subtracting the per cent pentosan in the cellulose from the cellulose value. Hence an error in either of these two values will affect the pentosan free cellulose value. The results of the Series 8 runs are plotted in Figure 9 and an inspection of the curve for pentosan in the cellulose indicates that the value for the first step is consistent while the value for the Cross and Bevan cellulose is a trifle high. The difference is not enough however to cause such a great difference in the pentosan free cellulose value. The only other variable that could affect this value is the pulp yield in the first step and the curve for pulp yields shows that the value obtained in the first step is consistent. The curves show that practically all the results obtained were consistent except two for the Cross and Bevan cellulose and the probable reasons for these variations have been discussed in the foregoing text.

3 - Summary

The results of the experiments using chlorine water

can be summarized as follows:

(1) Long continued chlorination is not as effective a means of delignification as alternate short chlorinations and sodium sulphite digestions. Sodium hydroxide can be used in the digestion but it does not give the lignin color reaction.

(2) About 3.5 per cent of lignin remains in the cellulose as residual lignin even after protracted chlorinations. This amount of lignin is about 11 per cent of the lignin present in the original stalk.

(3) The cellulose isolated by chlorination contains about 3 per cent of residual pentosan. This amount of pentosan is about 30 per cent of the pentosan present in the original stalk.

(4) The pentosans not in the cellulose, comprising about two-thirds of the total pentosans present in the original stalk, are rapidly removed during the chlorination.

(5) Some of the pentosan in the cellulose is removed by each chlorination at a fairly constant and gradual rate.

(6) Furfural-yielding bodies are not formed at the expense of the cellulose during the chlorination.

(7) Chlorine water appears to affect the removal of lignins and pentosans to the same extent as does chlorine gas.

(8) The successive steps required when using chlorine water are the same as for gaseous chlorine. Usually five chlorinations are sufficient in either case.

(9) The amount of Cross and Bevan cellulose isolated

with chlorine water is practically the same as the amount isolated with chlorine gas, and the chlorine water appears to have no detrimental effects on the pulps.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. O. R. Sweeney, Professor of Chemical Engineering, under whose direction this research was carried out, for his many helpful suggestions.

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Sugar is oxidized by nitric acid in the presence of a catalyst. To one part of sugar, ten parts of nitric acid (sp. gr. 1.4) and 0.002 parts of vanadic oxide are added. One and four-tenths parts of oxalic acid are obtained. The nitric acid and vanadium compounds may be used repeatedly. The nitrogen oxide vapors given off may again be applied.

2. Cash, R. R. and Sayler, G. Preparation of oxalic acid from corn cobs. Unpublished thesis. Library, Iowa State College, Ames, Iowa. 1922.

Oxalic acid was prepared by fusion with alkalies. The yields were only moderate, and control was difficult. Oxidation with nitric acid of 1.42 sp. gr. resulted in 50 per cent yields, and oxidation with 1.50 sp. gr. nitric acid gave 70 per cent yields of oxalic acid. Vanadium pentoxide was used as a catalyst.

3. Farlow, R. L. Preparation of oxalic acid from corn cobs. Unpublished thesis. Library, Iowa State College, Ames, Iowa. 1923.

Yields of 70 per cent of oxalic acid were obtained from corn cobs by oxidation with 1.5 sp. gr. nitric acid. Five parts by weight of acid were used to one part of cobs. A mixture of V_2O_5 and MoO_3 was used as a catalyst, and the reaction was forced by applying heat at the start. Sudden cooling at the moment the cobs were decomposed was essential in securing good yields.

4. Trexel, R. A. Further studies on the production of oxalic acid from corn cobs. Unpublished thesis. Library, Iowa State College, Ames, Iowa. 1923.

Yields of 100 per cent of oxalic acid were obtained from corn cobs by using 1.50 sp. gr. nitric acid in the proportion of five parts of acid to one part of cobs, and a mixture of V_2O_5 and MoO_3 as catalysts. The reaction is hastened by heating, and sudden cooling at the moment the cobs break into a yellow emulsion is necessary to secure high yields. It is necessary to let the reaction mixture stand several

hours before adding water, otherwise a yellowish white precipitate forms, and the yield of oxalic acid is low. Refluxing gives higher yields of oxalic acid than distillation, but less nitric acid is recovered.

5. Webber, H. A. Studies on the production of oxalic acid from corn cobs and stalks. Unpublished thesis. Library, Iowa State College, Ames, Iowa. 1925.

Yields of 70 per cent and more of oxalic acid were obtained from corn cobs by oxidation with 1.5 sp. gr. nitric acid. Either heating at the boiling point or the use of a catalyst gives about equally good yields. If both heating and a catalyst are used the reaction must be checked at a critical point to avoid destruction of the oxalic acid formed. The yield is increased if the reaction mixture is allowed to stand for several days after the heating period. The catalyst V_2O_5 , and some others, induce a very vigorous second reaction which must be closely controlled to obtain good yields.

6. Braconnot, M. E. De la transformation de plusieurs substances vegetales en un principe nouveau. Ann. Chim. Phys. 52:290-294. 1853.

Nitro-starch was prepared by dissolving starch in strong nitric acid and pouring the viscous translucent liquid into water. The resulting cheesy white substance was called "xyloidine".

Note: This name is now applied generally to any product that is made by dissolving a carbohydrate in nitric acid and pouring into water or sulphuric acid, or by dissolving in sulphuric acid and pouring into nitric acid.

7. Richardson, A. Action of heat on peroxide of nitrogen. Chem. Soc. Trans. 51:397-403. 1887.

The equilibrium between NO_2 and N_2O_4 at all temperatures between $20^\circ C$ and $140^\circ C$ was determined by the vapor density method. Above $140^\circ C$ no N_2O_4 exists and the equilibrium is between NO_2 and NO plus O_2 . At $620^\circ C$ NO_2 is completely dissociated into NO and O_2 . Vapor density tables for the range $20^\circ C$ to $620^\circ C$ are given.

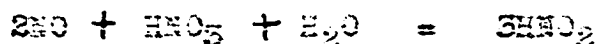
8. Lunge, G. and Berl, E. Zur Bestimmung der Oxyde des Stickstoffs und zur Theorie des Bleikammerprozesses. Zeitsch. Angew. Chem. 20:1717-1722. 1907.

In the case of mixtures of nitric oxide and air the most rapid oxidation occurs when the percentage of nitric oxide in the mixture is between 17-20 per cent.

In the case of the enriched air mixtures, the minimum time of oxidation is shown with gaseous mixtures containing 30-35 per cent of nitric oxide although these minimum values depend in each case upon the degree to which the oxidation is carried, e. g. 80 per cent of the nitric oxide in a 20 per cent mixture of nitric oxide and air requires a shorter time to oxidize than 80 per cent of the nitric oxide in a 17.5 per cent mixture, but 95 per cent of a 17.5 per cent mixture requires less time to oxidize than 95 per cent of a 20 per cent mixture.

9. Veley, V. H. The conditions of the formation and decomposition of nitrous acid. Proc. Roy. Soc. London, 52:28-55. 1893.

Nitric acid is somewhat unstable even at room temperature and nitrogen peroxide is evolved. Nitrous acid is stable to some extent in the presence of nitric acid. The reaction is



and is reversible. At moderate temperatures and for dilute nitric acid (below 30 per cent) the ratio of nitric to nitrous acid at equilibrium is about 9:1. At higher temperatures and with stronger nitric acids, the amount of nitrous acid is decreased.

10. Webb, H. W. Absorption of nitrous gases. Longmans, Green & Co., New York. 1923.

The capital costs of absorption systems for the recovery of nitrous oxides are considered under two heads; the small stoneware systems dealing with concentrated nitrous gases, and the large systems handling dilute gases.

The cost of a set of eight small stoneware towers capable of recovering 30 tons of nitric acid (as 100 per cent) per week is about \$10,000, while large tower systems for treating dilute gases cost two to three times as much, and in some cases the costs have been several hundred thousand dollars.

11. Cottrell, A. The manufacture of nitric acid and nitrates. C. Van Nostrand Co., New York. p. 105. 1923.

In the manufacture of nitric acid from Chili salt-petre, some nitrous oxides are formed. These are recovered in water absorption systems. The composition of the gases, the reactions involved in absorption, types of towers, types of packing, air lifts and other accessories, tower capacities, and concentration of nitric acid produced under various conditions are given.

12. Carpenter, C. D. and Babor, J. Concentrating dilute nitric acid solutions. Chem. & Met. Eng., 27:121-124. 1922.

The problem of concentrating dilute nitric acid is divided into two stages, preconcentrating and superconcentrating; i. e. bringing the acid up to 50 to 60 per cent by simple fractionation, and making acids of higher concentration. This second stage is necessary because nitric acid forms a constant boiling mixture at about 68 per cent. Vapor compositions above boiling solutions of known composition are given.

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The theory of the oxidation of ammonia to nitric acid is explained. Existing plants for the conversion are described in detail, and the production costs in the various necessary steps are given.

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Estimated costs are given of producing cyanamide, sulphate of ammonia, and nitrate of ammonia at the United States Nitrate Plant No. 2. The estimated costs are based on the actual results of a two weeks operating test of the plant at one-fifth capacity in January, 1919.

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The production of nitric acid from ammonia oxidation and from Chilean saltpeter is compared. Fixed charges, construction and operation costs for both processes are given. The cost of concentrating the dilute nitric acid from the ammonia oxidation process is a handicap to that process.

16. Milligan, L. H. The quantitative determination of reduction products of free nitric acid solutions. *J. Phy. Chem.* 28:544-578. 1924.

Analytical methods are described for the quantitative determination of reduction products of free nitric acid solutions: namely--nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, nitrous acid and salts of hydroxylamine, hydrazine and ammonia. A modified spiral gas-washing bottle is described which is claimed to bring the gas into very intimate contact with the absorbing liquid.

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18. Baly, E. C. C. and Chorley, J. C. Action of nitric acid on the ligno-celluloses. *Chem. News*, 71:226-228. 1895.

19. Gay-Lussac, J. L. Action de la potasse sur les matieres organiques. *Ann. Chim. Phys.* 41:398-402. 1829.

Cotton, sugar, woods and other carbohydrate materials were fused with caustic potash. Oxalic and other aliphatic acids were formed. Citric, malic and succinic acids were also fused and formed large amounts of oxalic acid, but benzoic acid resisted the action of the caustic potash.

20. Dale, J. English Patents 2767 and 3031. 1856. Abstracted from Hubbard, E. The utilization of wood waste. Scott, Greenwood Co., London, p. 84-104. 1902.

Oxalic acid is made by fusing one part of sawdust with a mixture of 1.5 parts of caustic potash, and one part of caustic soda. The alkalies are recovered and used over again.

The process is improved by treating the sawdust with a hot solution of soda or potash before fusing it with the caustic alkalies.

21. Possioz, L. Observations sur certaines differences d'action entre the potasse et la soude, a l'egard de diverses matieres organiques, dans la production des oxalates et des cyanures. *Comp. rend.* 47:207-10, 648-649. 1858.

100 parts of bran or other organic substances were fused with 100 parts of caustic potash and 500 parts of potassium manganate at 240°C to form oxalic acid.

The formation of ulmates, acetates, formates and carbonates was avoided by using the potassium manganate.

22. Thorn, W. Über gewinnung von Oxalsäure aus Sagespanen und aus Kleie, sowie aus Lignose. Dinglers polytech. J. 210:24-39. 1873.

Oxalic acid was produced by fusing sawdust or bran with lye in round iron pots. Sodium hydroxide was used alone, also mixtures of sodium and potassium hydroxides. Larger yields of oxalic acid were secured when the batches were fused in thin layers exposed freely to the air.

23. Erdmann, J. Über die Constitution des Tannenholzes. Annal. Chem. Pharm. (Suppl. Bd.) 5:223-232. 1867.

Erdmann observed the formation of acetic acid by the fusion of wood with potassium hydroxide. The acetic acid arises partly by saponification of acetyl groups, but mainly by oxidation. Better yields are obtained with potassium hydroxide than with sodium hydroxide, and with three parts of alkali than with one. The following yields were obtained with three parts of potassium hydroxide:

	:At 150°C :Acetic acid %	:At 200 to 250°C :Acetic acid %
Cane sugar	: 46.0	: 33
Hydrocellulose (from cotton)	: 19.5	: 29
Jute	: 15.0	: 37
Pine wood	: 18.0	: 28

24. Mahood, S. L. and Cable, D. E. Reaction products of alkali-sawdust fusion. J. Ind. Eng. Chem. 11:651-655. 1919.

Hardwood sawdusts were fused with sodium hydroxide. Optimum conditions were a three hour heating period at 230°C. Yields of about 20 per cent of acetic acid and 50 per cent of oxalic acid, based on the oven dry weight of the sawdust, were obtained under the optimum conditions.

25. Vaughn, K. E. Utilization of corn cob-alkali fusions in water softening. Unpublished thesis. Library, Iowa State College, Ames, Iowa. 1926.

Experiments were made in an effort to secure a water softening compound by fusing corn cobs with sodium hydroxide. For Ames water a residue containing 6 parts of sodium oxalate to 1 part of caustic would be satisfactory. The purpose of the oxalate is to remove the Ca-ions and of the caustic to remove the Mg-ions thus giving water of zero hardness. The organic matter present acts as a clarifying agent. The best result was 3 parts of oxalate to 1 part of caustic soda. This ratio would leave the treated water too caustic.

26. Heuser, E. Textbook of cellulose chemistry. McGraw-Hill Book Co., New York, p. 108. 1924.

27. Nechts, M. K. Nature of lignin. Biochem. J. 19:958-978. 1925.

A study of the methods of isolating pure lignin, and of the characteristics and properties of lignin obtained from various lignocelluloses. The most successful method of obtaining high alpha-cellulose, free from lignin, was to hydrolyze 5 grams of the ligno-cellulose material with 100 c.c. of 4 per cent sodium hydroxide solution for one hour under 10 atmospheres pressure, (180°C.)

28. Richter, G. A. U. S. Patent 1,678,230, July 24, 1928.

High alpha-cellulose is obtained from soda or sulphite pulp by a second treatment with a boiling solution of soda ash, caustic soda, or a mixture of the two alkalis at atmospheric pressure. An efficient heat recovery system is described which is stated to make the process economical.

29. Avram, M. H. The rayon industry. D. Van Nostrand Co., New York. p. 207. 1927.

The soda process, the sulphate process and the sulphite process are the three important methods of obtaining pulp from wood. Pulps produced by the soda process and bisulphate process are not usable for rayon manufacture because they lack solubility, uniformity and the necessary porosity or capillarity. Wood pulp prepared by the Ritter-Zellner modification (cooking with live steam) of the bisulphite process is the only pulp so far adapted to rayon making.

30. Bray, M. W. and Andrews, T. M. Factors influencing the properties of wood cellulose as isolated by the chlorination method. Paper Trade Journal. 76; 18:47-49. 1923.

as the time of chlorination was extended from 32 to 632 minutes the alpha-cellulose content of sulphite pulp (from spruce wood) decreased from 84 per cent to 55 per cent, while the beta-cellulose content increased from 1 per cent to 27 per cent. The gamma-cellulose content remained almost constant. The copper number increased from 4 per cent to 12 per cent, indicating the formation of non-resistant celluloses.

31. Ritter, G. J. Distribution of lignin in wood. J. Ind. Eng. Chem. 17:1194-1197. 1925.

The microscope was used in following the chemical reactions involved in the isolation of lignin from red alder and pine. Two kinds of lignin were found in both cases, about 75 per cent of the lignin being located in the middle lamella, and about 25 per cent in the other layers of the cell wall. The middle lamella lignins had a high methoxy content (about 11-14 per cent) while the other lignins had a low methoxy content (about 4.5 per cent). The lignins can be separated mechanically.

32. Schweitzer, P. Study of the life history of corn. Mo. Agr. Exp. Sta., Bul. 9. 1888.

Corn plants were taken for analysis in fourteen successive stages from June 11 to Sept. 24. Weights of single plants are given at Aug. 27, 338.8 grams, Sept. 10, 255.05 and Sept. 24, 229.0. Complete analyses of the parts of the corn plant at each stage are given.

33. Wiley, H. W. Composition of Maize. U. S. Dept. Agr. Bur. Chem. Bul. 50. 1898.

Analyses of the grain, stalks and cobs are given. The preparation and properties of corn meal, oil and other corn products are given.

34. Peterson, C. J. and Hixon, R. M. Chemical examination of the tissue of the cornstalk. J. Ind. Eng. Chem., Analytical Edition. 1:65-67. 1927.

The lignin, hemicellulose, and cellulose contents of the cornstalk were determined. The lignin fraction and hemicellulose fraction were investigated. The corn stalk contains approximately 50 per cent lignin, 27 per cent pentosan, and 36 per cent cellulose. No pectic material could be identified. The shell, pith

and vascular bundles were analyzed. The composition of these tissues does not vary greatly from that of the total stalk.

35. U. S. Tariff Commission. Investigation of the costs of production of oxalic acid in the United States and in the principal competing foreign countries. Govt. print. off. Washington, p. 4. 1925.